This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

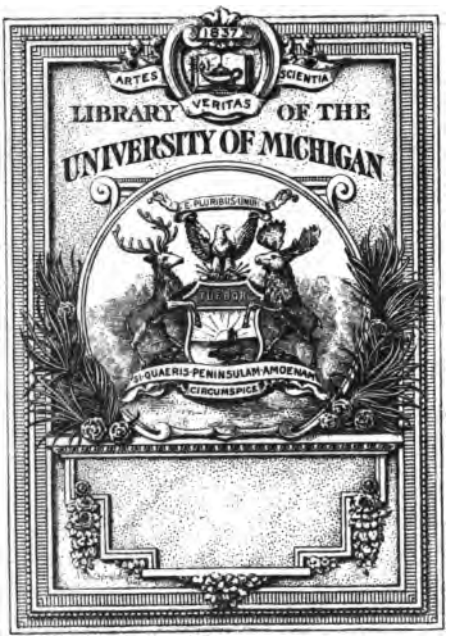
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

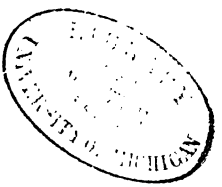
+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`


1837
ARTES
SCIENTIA
VERITAS
LIBRARY OF THE
UNIVERSITY OF MICHIGAN
E PLURIBUS UNUM
SI QUAERIS PENINSULAM AMOENAM
CIRCUMSPICE

Chemical Library
QD
1
.C518



THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

WILLIAM FRANCIS, PH.D., F.L.S., F.R.A.S., F.C.S.

VOLUME XVI. 1858.

LONDON:
PUBLISHED BY TAYLOR AND FRANCIS,
RED LION COURT, FLEET STREET.

PRINTED BY TAYLOR AND FRANCIS,
RED LION COURT, FLEET STREET.

THE

CHEMICAL GAZETTE.

No. CCCLXV.—January 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Investigation of Boron and its Affinities, especially its Affinity for Nitrogen. *By* F. WÖHLER *and* H. SAINTE-CLAIRE DEVILLE.

THE experiments made by the authors on the special affinity of titanium for nitrogen*, have induced them to pursue their investigations on boron in the same direction.

They employed the amorphous boron of Gay-Lussac and Thenard, prepared as follows. 100 grms. of fused boracic acid coarsely pounded are mixed with 60 grms. of sodium, and the mixture thrown into a cast-iron crucible at a strong red heat. The whole is covered with 40 or 50 grms. of fused common salt, and the crucible is closed. When the reaction is effected, the fused matter is stirred with an iron rod. Boron is formed, diffused in a perfectly fluid mass of fused boracic acid, borate of soda, and common salt; this is thrown red-hot into water acidulated with muriatic acid in a deep earthen pot. The whole is then poured upon a filter and washed with acidulated water until all the excess of boracic acid is dissolved, and afterwards with distilled water, which always carries a little pure boron through the pores of the paper. The boron must be dried upon tiles at the ordinary temperature, otherwise it might inflame and burn violently. This greenish, amorphous powder is a peculiar state of boron which may be easily converted into another more stable variety, and this takes place with evolution of heat and light, without any modification of colour and appearance; when heated in pure hydrogen, it takes fire in different places, exactly like oxide of chrome during calcination. With boron, however, the phænomenon is never observed through the whole mass, but especially in the parts which present the least cohesion. By this process the authors easily obtained from 500 to 600 grms. of boron.

Amorphous boron may be converted into crystallized boron by a very simple process. An earthen crucible is luted with amorphous boron, exactly as with charcoal, and a fragment of aluminium is put into it. At a high temperature the aluminium becomes charged with boron, which it allows to crystallize on cooling; the crystals are easily extracted by dissolving the aluminium either in sodium or in muriatic acid. When this experiment is performed with every precaution to prevent the access of the oxygen of the air to the

* See Chem. Gaz., Dec. 1, 1857, p. 449.

boron, the portion not transformed into crystalline boron, nevertheless undergoes a great alteration. It becomes white, and when treated with fused potash, evolves considerable quantities of ammonia, whence it must be concluded that boron absorbs the nitrogen of the air with as much avidity as titanium at a high temperature.

This is confirmed by the following experiments.

If amorphous boron be heated in a current of ammonia, it soon appears to become ignited; there is a distinct incandescence, and the ammonia is decomposed into nitrogen, which combines with the boron, and hydrogen, which is evolved and may be inflamed at the outlet of the apparatus. The nitruret of boron thus produced disengages torrents of ammonia with caustic potash, and appears to be identical with the compound of boron and nitrogen already described by one of the authors.

Boron, or even a mixture of boracic acid and charcoal, when strongly heated in the midst of a current of nitrogen, becomes entirely converted into white, infusible nitruret of boron; in the second case, the proportion of charcoal must be exactly that necessary for the reduction of the boracic acid.

Boron cannot consequently be heated in ordinary crucibles and furnaces, without being converted into nitruret in a reducing atmosphere. The only way to avoid this is by the employment of a lute composed of rutile and charcoal, which stops both oxygen and nitrogen; into this the crucible containing the boron to be heated is plunged.

In the production of crystalline boron with aluminium, the excess of the latter is often covered with small white crystals, which may be crystallized nitruret of boron, but the quantity was insufficient for investigation. It also appears that amorphous boron, when violently heated, becomes filled with crystals of graphitoid boron, either by a true transformation taking place under the influence of heat, or by the amorphous boron itself possessing a little volatility.

At a strong red heat amorphous boron takes fire in aqueous vapour, producing hydrogen and boracic acid, of which a part is volatilized with the water, whilst the rest, becoming fused, protects a great deal of the boron against the action of the aqueous vapour. The volatilized boracic acid crystallizes at a considerable distance from the point where the tube is heated, showing that it is not mechanically transported.

Boron absorbs sulphuretted hydrogen energetically, but without sensible production of heat. The sulphuret of boron formed is volatile in an excess of sulphuretted hydrogen, as boracic acid is volatile in water, so that in this case sulphuret of boron is obtained at a great distance from the point where it is produced. Berzelius, who prepared the sulphuret with sulphur, and Fremy, who obtained it crystallized by means of sulphuret of carbon, do not mention any such transportation, so that it seems to be dependent on the employment of sulphuretted hydrogen.

Muriatic acid is decomposed by boron with evolution of light even

at a low temperature. The chloride of boron produced may be condensed in a freezing mixture; it is identical with that obtained by passing chlorine over boron, or a mixture of boracic acid and charcoal. The bromide is produced in the same way, by means of boron and bromine.

The chloride and bromide of boron are not gases, as has hitherto been supposed, probably from the considerable tension of their vapour, which does not allow them to be easily separated from a gas with which they are always mixed when prepared by the processes of Despretz, Dumas or Poggiale. The chloride boils at 62° F. and the bromide at 194° F. The analyses lead to the formulæ

$$BCl^3 \text{ or } B\,Br^3 = 4 \text{ volumes.}$$

Iodide of boron could not be obtained by the direct union of boron and iodine; the small quantity produced in this case rather resembled an oxychloride or oxybromide of boron which we obtained in large quantities by the action of chlorine and bromine upon mixtures of boron and boracic acid, or boracic acid and charcoal. There is also an oxyfluoride of boron, which is always formed in preparing the fluoride of boron by the process of Gay-Lussac and Thenard.

Amorphous boron possesses curious properties, by which it approaches, as a reducing agent, both charcoal and the metals most nearly allied to the metalloids. The affinity of boron for chlorine is so great, that the metallic chlorides, such as those of mercury, lead, and silver, are reduced at a high temperature, with formation of chloride of boron, which is easily recognized by its thick and irritating vapours. Galena is also reduced by boron, with formation of lead and sulphuret of boron, the presence of which is easily recognized by means of a little water, which decomposes it with evolution of heat, and an abundant production of sulphuretted hydrogen.

The authors also call attention to the fact, that nitrogen, which is justly regarded as a passive and inert body, may become active under certain circumstances. The experiments of Gay-Lussac and Thenard upon nitruret of potassium, and of Despretz upon the action of ammonia upon metals, and especially upon iron, with the compounds produced by one of themselves between nitrogen titanium and boron, had already shown the intervention of nitrogen by an indirect course, in the composition of mineral substances. In their memoir on titanium and in the present paper, the authors have pointed out a direct action of nitrogen upon certain bodies, with all the phænomena which usually accompany energetic combinations, in the formation of compounds possessing great stability. They have also prepared nitruret of silicium.—*Comptes Rendus*, November 23, 1857, p. 888.

Chemical Investigation of the essential Oil of China Oranges (Essence de Mandarine). *By* S. DE LUCA.

The China or Mandarine orange (*Citrus bigaradia sinensis* and *Citrus bigaradia myrtifolia*) grows very abundantly in certain parts

of Calabria, in China, Algeria, and some European countries. The essential oil contained in the cells of the rind of the fruit does not occur in commerce, probably from the rather high price of the fruit, and it has not been examined chemically. The oil investigated by the author was prepared by expression, partly by himself, and partly by M. Anca of Palermo.

The essential oil, thus prepared, is limpid, and very fluid, and possesses a faint golden-yellow tint; its odour is very agreeable and different from those of lemon and orange; its taste is by no means disagreeable, and resembles that of orange-rind; it boils and distils exactly at 362°·4 F., leaving a very small residue, which, however, contains the minute quantity of matter which gave it its yellow colour. The distilled product is colourless, and has the same odour and taste as the crude oil; it is lighter than water, its density at 50° F. being 0·852 both for the first and last portions distilled; its density, as determined previously with another sample, was 0·8517 at 58°·6 F.

It does not appear to contain any oxygenated compound; its composition is represented by the formula $C^{20} H^{16}$. Three analyses gave,—

	I.	II.	III.		Calculated.
C	87·48	87·45	87·70	20	88·2
H	11·97	11·97	11·96	16	11·8

This essential oil is insoluble in water, to which, however, it imparts its aroma by agitation; it is soluble in about ten times its volume of alcohol, and dissolves in all proportions in sulphuret of carbon, which may be advantageously employed for its extraction; it is also soluble in æther and in crystallizable acetic acid, dissolves iodine, bromine, the resins, the oils, wax, phosphorus and sulphur, and mixes with the other essential oils.

Cold concentrated sulphuric acid gives it a red colour, but this disappears on the addition of water, giving place to a yellowish tint and turbidity; the same acid, when hot, decomposes and carbonizes it with evolution of sulphurous acid. Cold nitric acid does not act upon it, or colour it red, but it acquires the yellowish tint of the crude oil; the same acid, when hot, attacks it readily, with evolution of nitrous vapours, and on the addition of water, a yellow, insoluble and nearly solid matter separates.

When cold, it absorbs dry muriatic acid gas, and acquires a brown colour; concentrated muriatic acid at the ordinary temperature gives it a brown colour, and after two or three days' contact, gives rise to a crystallized matter of peculiar odour, the composition of which corresponds exactly with the formula $C^{20} H^{16}$, 2HCl. This compound, produced by the direct combination of the essential oil with muriatic acid, and representing the bimuriate, is solid, and forms small, transparent lamellæ, which are fusible and volatile, insoluble in water, and soluble in alcohol and æther.

Mixed with alcohol and nitric acid, the essential oil gives origin to a crystallized matter, probably the hydrate; the small quantity obtained did not allow a complete examination to be made.

This essential oil has the remarkable property of presenting the phænomenon of epipolic dispersion, discovered by Mr. Stokes, when it is looked at under certain incidences of light, exactly like the solutions of sulphate of quinine which present a characteristic blue tint upon their surface. The same coloration is presented, not only by the pure essential oil, but also by its alcoholic, acetic, and ætherial solutions, &c. The crude essential oil does not present this phænomenon, probably on account of the presence of the yellow matter.

Lastly, the oil deviates the plane of polarization to the right, and this power of deviation was always found to be $=111{\cdot}5$, tint of passage, whence the rotatory power corresponding to the red ray would be equal to $85{\cdot}5$. This rotatory power is greater than that of the essential oils of turpentine, lemon, orange, and bergamot, which have all the same composition.

Thus this essential oil is defined by the constancy of its physical properties, density, boiling-point, and rotatory power, as well as by that of its chemical properties. It is the first known example of such homogeneity in a natural essential oil.—*Comptes Rendus*, November 23, 1857, p. 904.

On the Preparation of Manganese. By C. Brunner.

In continuing his experiments on the reduction of manganese, the author has made some further observations, which he publishes as a supplement to his previous memoirs.

He first describes the preparation of protochloride of manganese. When this can be obtained as a residue of manufacture, of course such crude solutions of protochloride of manganese may be made use of directly. Otherwise it is prepared as follows:—

Powdered black oxide of manganese, moistened with a very small quantity of water, is calcined in an earthen crucible. The residue, when cold, is treated in a retort with three times its weight of common muriatic acid, and the mixture is digested gently for 24 hours. It is then evaporated to dryness in an earthen capsule; the brown saline mass obtained is broken up, and roasted at a bare red heat, during which operation it is frequently stirred with an iron spatula.

The gray powder thus obtained is then extracted with water. The pale rose-coloured solution produced contains no trace of iron, but retains some zinc and cobalt; the presence of the latter is shown by the fact, that a small portion, when evaporated in a porcelain capsule, acquires a bluish colour immediately before it becomes perfectly dry.

To get rid of these impurities some acetate of soda is added to the solution, which is then treated with sulphuretted hydrogen gas. A precipitate is formed, which is at first dingy white, and afterwards becomes brownish; by the aid of heat this separates more completely and falls to the bottom in black flakes. A filtered portion of the fluid is then again tested for cobalt by evaporation. If

a bluish colour still occurs, the addition of acetate of soda and the treatment with sulphuretted hydrogen must be repeated.

If cobalt be no longer shown by testing, the fluid is examined for sulphuric acid, and if this be present, it is thrown down by chloride of barium. This is necessary, as otherwise in the reduction, the metal might contain a small amount of sulphur. The solution filtered from the precipitate of baryta is then evaporated to dryness, and the pale rose-coloured salt thus obtained is fused in a crucible; this takes place at about the melting-point of chloride of calcium. Too strong a heat must be avoided, as otherwise a portion is volatilized, or perhaps partially decomposed.

The fused saline mass is poured out upon a plate of stone or metal, and immediately after cooling pounded into a coarse powder and preserved in well-stoppered bottles, as it attracts moisture very readily.

To reduce the metal, the protochloride of manganese thus prepared is mixed with an equal weight of pounded fluor-spar by agitation in a flask, and divided into portions of about 15 grms. each placed in a small corked bottle. Into each bottle about 3 grms. of sodium freed from adherent naphtha is put, in fragments of the size of a pea.

A Hessian crucible is then heated to a slight red heat, and the contents of the bottles are thrown into it one by one. After each addition the crucible is lightly covered, and the next portion is not thrown in until the reduction, which takes place with noise and flame, is completed.

When a crucible capable of containing 4 ounces of water is employed, and 10 to 12 portions have been thrown into it, the mass is covered for more certainty with about 1 ounce of fused and coarsely pounded chloride of sodium. The fire is then strengthened by blowing so as to give a moderate white heat, that is to say about the temperature required for the fusion of cast iron. This is continued for 10 minutes.

The crucible is then allowed to cool slowly, and on breaking it the metal is found at the bottom of the crucible, beneath the slag, in the form of a perfectly fused, roundish regulus.

Although the author has effected all his reductions with the quantities above described, there is no doubt that the same process may also be employed on a larger scale.

The quantity of metal obtained is indeed not what might be expected from calculation, nor is it always the same. In such operations it is, of course, impossible to prevent a considerable portion of the sodium from being partly evaporated and partly burnt by the heat of reduction. With a little practice, however, the maximum that is to be obtained, may be reached. From the author's observations, he values this at 65 against 100 of sodium employed.

To combine small fragments of manganese into larger masses, or to work up imperfectly reduced specimens, the following is the best mode of proceeding:—

The metal is pounded in a steel mortar into a coarse powder, this is mixed with twice its volume of anhydrous chloride of sodium, and exposed to a white heat for 10 minutes in an earthen crucible.

A refusion of this kind is always advisable. Metal which has not been fused a second time acquires small spots on its surface when polished and kept for a considerable time, and these appear to be due to impurities. By a second fusion the latter pass into the slag.—Dingler's *Polytechn. Journ.*, cxlvi. p. 44.

On Piperic Acid. By Prof. von Babo *and* E. Keller.

Piperine is placed in a flask with an alcoholic solution of potash, and the flask connected with a condenser so that the products of the action flow back into the flask, which is heated on the water-bath. (For 1 part piperine 3 parts of hydrate of potash and 12 to 20 absolute alcohol are taken.) A decomposition of the piperine takes place, lustrous scales are formed in the brown liquid, and at the same time the characteristic odour of piperidine is observed. This treatment is continued until no more crystals are formed (which for 30 grms. piperine requires about 12 hours), and the piperine is then completely decomposed. The crystals are separated from the mother-liquor by means of a linen filter. The mother-liquor contains piperidine, for by distilling it and collecting the distillate in hydrochloric acid, the hydrochlorate of that base was obtained. The residue in the retort contains substances which appear to be identical with the products of the action of potash on absolute alcohol.

The crystalline plates consist of the potash-salt of a new acid, which the authors name

Piperic Acid.—The potash-salt may be purified by repeated crystallizations and the use of animal charcoal. Or if this method be not quite successful, the solution is neutralized by acetic acid, and a few drops of acetate of lead solution added, which produces a feeble brownish precipitate. The solution is heated to boiling, and sulphuretted hydrogen passed through, to remove traces of lead. After filtration and concentration, the potash-salt is obtained in yellowish-white crystals. To obtain the acid, these are dissolved in water, and decomposed by either sulphuric, hydrochloric, or acetic acid, which liberate the acid in the form of a voluminous gelatinous precipitate, which is seen under the microscope to consist of extremely fine needles. The precipitate is collected on a filter, washed, and then dried *in vacuo* over sulphuric acid. On crystallization from alcohol, it forms fine interwoven needles of a yellowish colour which is peculiar to them.

The acid is almost insoluble in water, readily soluble in boiling absolute alcohol, from which it crystallizes on cooling. It melts at 302° and sublimes at 392° F.: a brown residue remains, and the sublimate has the odour of cumarine. The acid scarcely reddens litmus, but forms with bases well-characterized salts.

Treated with weak nitric acid, piperic acid forms an orange-coloured nitro-compound. By sulphuric acid it is decomposed with

formation of the violet colour characteristic of piperine when similarly treated. With chlorine, iodine, and bromine substitution products are obtained, which await investigation. With pentachloride of phosphorus, it yields oxychloride and a substance which is deposited in vermilion-coloured crystals.

The analysis of the acid gave—

	I.	II.	III.	IV.
C	=66·88	66·08	66·74	66·39
H	4·80	4·83	5·06	5·14
O	28·32	29·09	28·20	28·47

From these results the formulæ may be calculated:—

C 50	=300	66·37	C 50	=300	66·67	C 26	=156	67·24
H 24	24	5·31	H 22	22	4·89	H 12	12	5·17
O 16	128	28·32	O 16	128	28·44	O 18	64	27·59

The formation of piperic acid may be expressed by the following equation:—

$$\underset{\text{Piperine.}}{C^{70}H^{40}N^{2}O^{12}} + 4HO = 2(\underset{\text{Piperidine.}}{C^{10}H^{11}N}) + \underset{\text{Piperic acid.}}{C^{50}H^{22}O^{16}}$$

The authors do not decide whether the acid contains 22 or 24 equivs. of hydrogen. From the large number of equivalents of hydrogen, and its small per-centage, the analyses furnish little help in the decision. Analogy with other acids renders 24 equivs. more probable, but the decomposition of piperine points rather to 22. They also consider the acid to be bibasic, on the ground that if monobasic, it would contain an uneven number of equivalents of carbon.

Piperate of soda is obtained by dissolving the acid in boiling caustic soda; on cooling, the salt is deposited as a white crystalline powder. It is so insoluble in cold water that it might serve as a test for soda.

Piperate of ammonia is formed by mixing concentrated aqueous ammonia with the acid, filtering and allowing to stand. It crystallizes in colourless brilliant plates which strongly resemble cholesterine. Exposed to the air it decomposes, ammonia is given off, and the subtance becomes yellow from separation of acid.

Piperic acid forms with baryta and lime insoluble salts. It also combines with the metallic oxides to form salts which are mostly insoluble. Piperate of piperidine forms colourless lamellar crystals of splendid silken lustre. On exposure to the air, it undergoes a similiar decomposition to the ammonia-salt. Piperic æther forms colourless crystalline plates. It melts at 158 to 160° F., and decomposes at a higher temperature with the production of a horrible acroleine smell.

The treatment of alkaloids with alcoholic potass appears to afford an important means of arriving at their constitution. Preliminary experiments with other alkaloids, especially cinchonine, show that the decomposition is different to that by fusing them with alkalies. And, as the action is less energetic, it may be expected that the products obtained stand in simpler relation to the bodies from which they are obtained.—*Journ. für Prakt. Chemie*, vol. lxxii. p. 53.

On Phloretic Acid. By Professor H. Hlasiwetz.

In a previous memoir* the author stated that phloretine, a product of the splitting up of phloridzine, is decomposed under the influence of an alkali, into an acid, which he calls phloretic acid, and a sweet body (phloroglucine) very similar to orcine. This decomposition takes place without the formation of a third body, and we have the process expressed by a similar equation as when the alcohol and the acid are regenerated from a compound æther.

From the author's first experiments, he regarded phloretic acid as monobasic. It has, however, 1 equiv. less hydrogen than is expressed by the formula $C^{18} H^{10} O^5$, HO, and it saturates 2 equivs. of base.

The formula of phloretic acid, as the author now finds, is $C^{18} H^{10} O^6$; it does not belong to the group of lichenic acids, as he formerly supposed, but to the series of salicylic acid.

Pure Phloretic Acid is homologous with salicylic acid; it is very slightly soluble in cold, very soluble in hot water, but dissolves most readily in alcohol and æther, and crystallizes from the latter solution in very beautiful, large, voluminous crystals. The crystals obtained from the ætherial solution are monoclinohedric.

The author's analyses of phloretic acid are as follow:—

C	65·07	65·05	64·84	65·00	64·77	18	= 108	65·06
H	6·04	6·23	6·37	6·30	6·42	10	10	6·04
O	..	..	..	..	..	6	48	29·92

Copper Salt, $C^{18} H^9 O^5$, CuO.—A solution of the acid baryta salt was decomposed by acetate of copper. A voluminous green precipitate was immediately produced, and this was extracted with a large quantity of water. On evaporation the salt crystallized in beautiful emerald-green prisms. To facilitate the solution of the precipitate a little acetic acid may be added.

The salt when once crystallized is difficult of solution in water even when boiling, nor does alcohol dissolve any more of it. Æther however dissolves it completely. At 212° F. it parts with its water of crystallization (equiv. calculated 8·38, found 8·56). Analysis:—

C	34·91	34·88	18	= 108
H	4·57	4·89	9	9
O	18·34	..	5	40
CuO	20·18	20·51	1	39·7

Baryta Salt, $C^{18} H^8 O^4$, BaO, HO.—This salt is produced in exactly the same way as the neutral baryta salt of salicylic acid. From a concentrated boiling solution of the acid salt, the addition of very concentrated baryta-water throws down a voluminous precipitate, which is quickly pressed, and recrystallized from a small quantity of boiling water. The salt is usually obtained in verrucose crystalline groups. The solution has an alkaline reaction and is decomposed by carbonic acid. The salt loses its water of crystallization with difficulty. When dried at 212° F. it gave numbers

* Chem. Gaz. vol. xiv. p. 81.

which lead one to conclude that it still contained 5 equivs. Analysis:—

C	31·60	18	31·19
H	3·74	9	3·75
BaO	44·03	1	44·25

Dried at 212° F. ($C^{18} H^{9} O^{5} [BaO]^{2}$).

C	34·40	18	34·81
H	3·00	9	2·90
BaO	49·60	2	49·40

Lime Salt.—If a concentrated solution of the acid potash salt be decomposed by a saccharine solution of lime, a precipitate of neutral salt is produced as soon as the reaction begins to be alkaline. When heated with water, filtered and evaporated under the air-pump, it crystallizes in soft, shining laminæ. It is decomposed by carbonic acid, and has an alkaline reaction.

Zinc Salt.—A neutral zinc salt appears to be formed during the decomposition of phloretic acid with an excess of carbonate of zinc at the boiling-point. The acid salt is dissolved, and crystallizes rapidly on cooling; the residue contains a great portion of the acid employed, combined with the oxide of zinc.

Copper Salt, $C^{18} H^{9} O^{5}$, 2CuO.—The acid copper salt dissolves pretty readily in æther, with an intense emerald-green colour. If such a solution be long heated, or allowed to boil for some time, very beautiful, shining, bluish-green spangles soon separate, giving the fluid an opalescent appearance. These are the neutral salt. They were filtered and washed with æther. They are almost insoluble in alcohol and æther. Water dissolves them sparingly when hot. They were at first dried at 212° F., but appeared still to retain 2 equivs. at this temperature. When dried at 248° F. they gave—

C	45·51	18	45·68
H	4·10	9	3·80
O	..	5	..
CuO	..	2	32·29

Lead Salt, $C^{18} H^{9} O^{5}$, 2PbO.—When a solution of phloretic acid is saturated with carbonate of lead and filtered, and the hot solution is mixed with basic acetate of lead, a heavy voluminous, white precipitate is thrown down; this must be quickly filtered and washed. When dried at 248° F. it agrees pretty well with the formula $C^{18} H^{9} O^{5}$, 2PbO, but it is slightly decomposed even by washing, and has a variable composition according to the mode of preparation. Analysis:—

C	27·00	27·53	18	28·39
H	2·95	2·89	9	2·37
PbO	58·28	58·30	2	58·72
O	..	..	5	..

If the salt be produced in the cold, it is richer in oxide of lead and nearly corresponds with the formula $C^{18} H^{9} O^{5}$, 3PbO + HO.

Phloretic Æther, $C^{18}H^{9}O^{5}, C^{4}H^{5}O$.—The preparation of phloretic æther is effected without difficulty by the decomposition of iodide of æthyle with a salt of phloretic acid. The experiment was made with the silver and potash salts. If phloretate of potash be kept with a little alcohol and an excess of iodide of æthyle in a closed tube for several hours at the temperature of boiling water, the whole dissolves uniformly at first, but at the end of the operation nearly all the potash is found separated as iodide of potassium.

The somewhat yellowish fluid was first of all freed from the excess of iodide of æthyle and alcohol on the water-bath, and the residue was then heated in the oil-bath. When the temperature had reached 392° F., nothing more was driven off, and the residue could then be heated to 482° F. without boiling. It was distilled by the open fire, and the distillate agitated with silver and rectified. It was then kept for some time at 446° to 464° F. in the oil-bath, to remove every trace of subsidiary constituent. It did not boil even at 509° F., and was at last heated again over the spirit-lamp, and distilled.

This rectified product is pure phloretic æther; it is colourless, thickly fluid, of a weak odour, and an acrid taste. Its boiling-point is above 509° F. It cannot be inflamed, produces a fatty spot on paper, and diffuses an irritating odour when heated on platinum; it dissolves in alcohol and æther, and is again separated by water. Analysis:—

C	68·15	22 =	132	68·04
H	7·55	14	14	7·22
O	..	6	48	25·74

The optical properties of this æther were compared by Dr. Grailich with those of salicylic æther. Both fluids possess the same power of refraction for a ray in the orange; but on the whole the dispersive power of salicylic æther is greater than that of phloretic æther.

Binitrophloretic Æther, $\left.\begin{matrix} C^{18}H^{7}(NO^{4})^{2}, O^{5} \\ C^{4}H^{5}O \end{matrix}\right\}$.—If phloretic æther be brought in contact with nitric acid of the ordinary strength, it becomes converted without any violent reaction into a golden yellow oil, which in a short time solidifies in a crystalline form. When washed with water and recrystallized from alcohol, it forms light yellow, somewhat bitter crystals, which are readily soluble in alcohol and æther, but very sparingly in cold water. Analysis:—

C	46·76	22	46·44
H	4·92	12	4·22
N	9·62	2	9·87

Phloretate of Oxide of Amyle, $\left.\begin{matrix} C^{18}H^{9}O^{5} \\ C^{10}H^{11}O \end{matrix}\right\}$.—Iodide of amyle and a very concentrated solution of phloretate of potash were treated in the same way as for the preparation of the æthyle compound. The fluid was kept boiling for a long time on the oil-bath. The decomposition takes place rather more slowly than in the preceding case, but just as completely.

After cooling, the greater part of the iodide of potassium separated by crystallization, and the fluid was poured away and distilled off. During this more iodide of potassium separated, and at last, when nothing more passed at 284° F., there remained a heavy, thick fluid. The contents of the retort were treated with hot water; the iodide of potassium was thus washed out, and the æther separated as a heavy oleaginous mass, which was still coloured. The last remains of water were expelled by heat, a small quantity of iodine was removed by silver, and when it had been kept for a long time at 284° F. without any evaporation taking place, it was heated to a higher temperature and finally distilled by the open flame. The rectification of this æther is a very troublesome operation, on account of its very high boiling-point, which is above 554° F., and in consequence of the rapid condensation and return of the product, it must be effected in a strongly bent tube. The distillate is colourless, very thickly fluid, of a weak, somewhat rancid odour, and a sharp and acrid taste; it makes greasy spots on paper. The solubility is the same as with the æthyle compound. Analysis:—

C	71·42	28	71·18
H	8·43	20	8·47

The amylic æther furnishes a crystallized nitro-compound, which agrees exactly in its properties with that of the æthylic æther.

[To be continued.]

On Methylophosphorous Acid. *By* Dr. Hugo Schiff.

If the protochloride of phosphorus, $\left.\begin{matrix}P\\Cl^3\end{matrix}\right\}$, representing phosphorous acid, $\left.\begin{matrix}P\\H^3\end{matrix}\right\}O^6$, be dropped into wood-spirit as long as any action takes place, and the fluid be left standing for several hours in a warm place until the muriatic acid and the excess of wood-spirit are driven off, there remains

Methylophosphorous acid, $P\left\{\begin{matrix}C^2H^3\\H^2\end{matrix}\right\}O^6$, in the form of a tenacious, nearly colourless, and very acid syrup. In attempting to concentrate it further, it becomes decomposed into wood-spirit and phosphorous acid.

The salts of this acid are obtained by saturating the free acid with carbonates of the bases. They must be evaporated only at a very gentle heat, as otherwise they are decomposed into methylic alcohol and phosphites. They are all amorphous masses, very soluble in water, less so in alcohol, and insoluble in æther.

The *monomethylophosphites of lime and baryta* have the compositions $\left.\begin{matrix}PC^2H^3\\H,\ Ca\end{matrix}\right\}O^6$, and $\left.\begin{matrix}PC^2H^3\\H,\ Ba\end{matrix}\right\}O^6$. The baryta salt is anhydrous. It is less soluble in water and alcohol than the lime salt. The lead salt is very decomposable.

A solution of the lime salt gives a white precipitate with nitrate of mercury. Perchlorides of copper and iron produce no precipitate. The addition of nitrate of silver produces a white precipitate, from which silver is very soon reduced.—Liebig's *Annalen*, ciii. p. 164.

ANALYTICAL CHEMISTRY.

On the behaviour of Molybdate of Ammonia to Silicic Acid. *By* Dr. W. Knop.

The author has already stated* that molybdate of ammonia gives with silicic acid a yellow precipitate exactly similar to that produced by it with phosphoric acid. He now describes the conditions under which this yellow precipitate appears in the presence of silicic acid, and the mode in which the presence of phosphoric acid, which might give rise to error, may be prevented.

Crystallized bicarbonate of potash was ignited in a silver capsule, dissolved in water, and filtered. Of this, one-third was boiled in the silver capsule with pure silicic acid, until it was almost entirely dissolved; the solution was filtered through the same filter through which the solution of carbonate of potash had previously passed.

The silicic acid was prepared by passing fluoride of silicium into water. After being dried in the air, it was boiled with water containing muriatic acid, and washed for a long time with water.

A concentrated solution of molybdate of ammonia was also prepared by dissolving the dry salt in ammonia; it was so concentrated that molybdic acid was thrown down from it on the addition of concentrated sulphuric acid.

Equal quantities of the solutions of carbonate of potash and silicic acid were then poured into beakers, and 2 cub. cents. of the solution of molybdate of ammonia were added to each fluid by means of a pipette. To each fluid there was also added an equal volume of a perfectly saturated solution of muriate of ammonia; they were then greatly supersaturated with drops of concentrated nitric acid, and boiled.

The solution of potash *free from silicic acid* only exhibited a yellowish tint.

The *solution of silicic acid* threw down a thick citron-yellow precipitate.

The addition of muriate of ammonia appears to be a necessary condition for the production of the yellow precipitate.

Further experiments showed that the solution of molybdate of ammonia need not be by any means so concentrated as above described. At any rate, silicic acid may readily be mistaken for phosphoric acid. If the solution of molybdic acid in nitric acid be very dilute, it appears not to give the yellow precipitate with silicic acid so easily.—*Chemisches Centralblatt*, Dec. 2, 1857, p. 861.

* See Chem. Gaz. vol. xv. p. 439.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Ultramarine. By J. G. GENTELE.

THE author has given a description of the manufacture of ultramarine, of which the following is an abstract.

The manufacture consists of two parts.

I. The preparation of green ultramarine.

II. The conversion of green ultramarine into blue.

I. *Preparation of green Ultramarine.*—The raw materials at present in use are,—

1. An alumina silicate (kaoline).
2. Calcined sulphate of soda.
3. Calcined carbonate of soda.
4. Sulphide of sodium.
5. Sulphur.
6. Charcoal or coal.

As an alumina silicate kaoline is used, or a white clay with a similar composition. A certain admixture of lime and magnesia is not injurious, but a greater quantity of oxide of iron than 1 per cent. is objectionable. The clay is elutriated in order to separate it from mechanical impurities as much as possible. The elutriated clay is dried and ignited, and is then easily reduced to a fine powder.

Sulphate of soda and *carbonate of soda* are obtained sufficiently pure from the chemical manufactories; both are powdered and sieved. In cases where the sulphide of sodium is obtained in the liquid form, it is evaporated in cast-iron pots, or iron pans, and the residue powdered. In using it, it is calculated as monosulphide of sodium. *Roll-sulphur* is used and is kept in stock in the form of fine powder.

Wood-charcoal or *coal* are used; of the latter, a non-caking coal, and one that leaves little ash, is preferred. Both sorts of carbon are finely powdered before being used. In preparing the mixture, it is essential not only that the substances be in the right proportions, but also that they be very intimately mixed. With dry materials the substances are weighed, then well mixed in a trough by means of a shovel and sieved, and the shoveling and sifting frequently repeated. Where solutions of sulphate of soda, carbonate of soda, and sulphide of sodium are used, the kaoline is introduced into the solution, and the whole evaporated to dryness, the charcoal powder being added from time to time. The dried mixture is then gently ignited in a reverberatory furnace, powdered, and mixed as intimately as possible by shoveling and sifting.

The proportions in which the raw materials are used, are various in each case.

1. Soda, either as sulphate or carbonate, must be present in such quantity that half the silica of the clay may be neutralized by it.

2. There must be a sufficient quantity of soda and sulphur to form a certain quantity of bi- or polysulphuret.

3. There must be an excess of sulphur and sodium present as

monosulphuret, besides the quantity which, according to the best analyses, is necessary to form green ultramarine with the silica and clay present in the mixture.

The French manufacturers use soda as soda-salt, the Germans, on the other hand, use only sulphate of soda, or a mixture of sulphate of soda, and carbonate of soda. By using sulphate, more carbon and no sulphur is required; by using carbonate of soda, less carbon and much sulphur is necessary; and hence the Germans work somewhat more cheaply than the French.

The three following mixtures may be taken as a sample:—

	I.	II.	III.
Kaoline (anhydrous).....	100	100	100
Calcined sulphate of soda..	83—100	..	41
Calcined carbonate of soda.	..	100	41
Carbon	17	12	17
Sulphur.....	..	60	13

100 parts calcined carbonate may be replaced by 80 parts calcined sulphate; 100 parts of the latter by 60 parts dry sulphide of sodium.

The ignition is effected in crucible-formed vessels or pots, in furnaces whose construction is similar to the small porcelain furnaces, at a high and uniform temperature, and with as complete exclusion of air as possible. The mixture is placed in the pots by means of small shovels, and pressed firmly by wooden clubs. The temperature to which the pots are gradually raised is between a bright red and a white heat: the duration of a firing varies from 7 to 10 hours; the furnace is then allowed to cool, and the contents of the crucible appear then as a caked mass of a gray or often yellowish-green appearance; it is then frequently watered. In this state the ultramarine appears as a light spongy mass, consisting of small and large porous pieces, which are ground in mills to the finest powder; the powder is then washed, and afterwards dried. After the product has been again powdered and passed through sieves, it may be either sold as *green ultramarine*, or used for conversion into blue ultramarine.

II. The *preparation of blue Ultramarine* from green offers no difficulties. At present it is generally effected by roasting green ultramarine with sulphur at a low temperature, and under access of air, so that the sulphur may burn to sulphurous acid. At the same time a part of the sodium oxidizes, and is then extracted from the ultramarine as sulphate of soda. The sulphur contained in the green ultramarine remains completely behind, but combined with less sodium.

In the German roasting-process small iron cylinders are used which are built over a furnace. The posterior end of the cylinder is fixed, and is provided with a hole in which the axis of a stirrer may be placed. The anterior part may be easily taken away; it has an opening for the projecting axis of the stirrer, a small opening below, and a larger one above, which serve for adding sulphur, and which may be closed by bolts. At the upper side of the cylinder

there is another small opening for the exit of sulphurous acid. The cylinder provided with the stirrer is filled with 20 to 30 pounds of green ultramarine, closed, and heated in the furnace. From time to time the axis is turned in order to heat the ultramarine uniformly. When it has been heated so far that a piece of sulphur thrown into the opening of the cylinder spontaneously takes fire and burns, the fire is moderated, about a pound of sulphur is added, the stirrer is turned, and the filling-hole left open in order to allow the sulphur to burn off. The mass is turned slowly until no more sulphur-vapours escape. This treatment with sulphur is repeated until a sample exhibits the highest purity and intensity of the blue colour. In some manufactories the roasting is not finished at once, but the product, before it has become quite blue, is once more washed, ground, mixed, and sieved. By this means a more uniform blue is attained, because no lumps remain which may be greener internally than externally. After roasting again, washing, drying, and sifting, this ultramarine will be of the best quality. The brighter sorts are mostly produced by the addition of white substances.

In the French roasting-process, a sort of muffle-furnace is used, or reverberatory furnaces so constructed that the flame cannot play on the mixture. The ultramarine is spread out in a uniform layer from 1½ to 2 inches in height, and heated with the door closed until a piece of sulphur thrown in, immediately begins to burn. A shovelful of powdered sulphur is then added, and the mass kept stirred with iron rakes until the sulphur is burnt off. The operation is repeated until the shade and intensity of the blue colour ceases to improve.

When blue ultramarine is washed by displacement, a saturated sulphate of soda solution is obtained, which may be used in the manufactory after the iron has been precipitated by lime. Ultramarine by being burned with sulphur increases somewhat in weight, but on washing loses a small per-centage.

When the washing has been imperfectly performed, the ultramarine gradually cakes together in the casks in which it is preserved.—Dingler's *Journal*, cxlii. p. 351.

On the Action of Carbonate of Soda upon Cast Iron at high Temperatures. *By* C. Tissier.

Different people have expressed their astonishment that the mass of the wrought-iron tubes employed in the manufacture of sodium is never converted into cast iron, although the mixture used in the preparation of sodium is very rich in carbon. In consequence of this the author made some experiments, in the course of which he became convinced that iron undergoes no change at all by the action of such a mixture at the temperature at which sodium is produced. By exposing fragments of cast iron to the long-continued action of this mixture, he even succeeded in converting it into steel and afterwards into malleable iron, without any change of form. These results induced him to investigate the action of carbonate of soda upon wrought and cast iron at the melting-point of the latter,

and in this way he found that carbonate of soda really has no action upon wrought iron (which is a fortunate circumstance for the manufacture of sodium), but that it extracts the carbon and silicium from cast iron, and thus converts it into malleable iron which is no longer fusible. When gray pig iron (that employed by the author contained 6·6 per cent. of silicium and graphitic carbon) is kept for several hours in an excess of carbonate of soda which is fused at a bright red heat in a crucible, the following circumstances are observed:—

When the heat is sufficiently raised, the mass boils up, and large bubbles of carbonic oxide gas are evolved, and burn with a yellowish flame. The yellow colour is not so vivid as to give rise to a supposition that a reduction of sodium takes place. When no more carbonic oxide gas is evolved, the application of heat is stopped, the iron is taken by means of tongs out of the fused carbonate of soda, and cleaned with a hammer or with water from the small quantity of this salt which adheres to it. Its surface is now completely eaten away; the fragments are not misshapen; they bend under the hammer, and may be wrought both cold and hot; the granular fracture of the cast iron has disappeared, and become replaced by a fibrous-crystalline texture; the mass has also become vesicular, and the cavities are filled with white globules of silicate of soda, the silicic acid of which has been produced from the silicium of the pig-iron.

The iron thus treated is scarcely attacked by muriatic acid in the cold, and is only dissolved by it very slowly with the aid of heat. Dilute nitric acid certainly acts more energetically upon it, but still far less rapidly than upon ordinary wrought iron, and especially upon cast iron. As a matter of course the action of the carbonate of soda is not confined to carbon and silicium, but phosphorus and sulphur also must be extracted thereby from the iron. Perhaps (but this the author still proposes to investigate) the iron takes up a little sodium, and by this means not only is not injured, but actually acquires properties on account of which the dealers willingly buy the cylinders which have become unserviceable in the manufacture of sodium. If this should not prove to be the case, we must suppose that a quantity of anhydrous soda equivalent to the amount of carbonic oxide gas evolved is produced.

It is well known that cast iron may be converted into malleable iron by cementation with substances which are rich in peroxide of iron, and this process is made use of daily by many French manufacturers for small cast iron objects, the hammers of percussion locks for example. Perhaps the same object might be attained more easily and better by the action of fusing carbonate of soda; at least this process would be preferable, in as far as the object might be taken from time to time out of the fused mass in order to see whether it had been treated long enough, which cannot be done when the cementing powder is employed. The author hoped to be able to apply the treatment of cast iron with carbonate of soda to large objects, which up to this time have only been made of wrought iron; but the slowness with which the operation goes on when the object is of considerable thickness, and the porosity of the iron thus

obtained, which would render the cooperation of the hammer necessary in order to bring the parts close together, necessitate the introduction of some modification in the process, which may get rid of these two disadvantages. Nevertheless, it must be observed, that cast-iron objects, and especially such as are not very large, acquire a greater solidity by treatment with carbonate of soda, so that they are no longer liable to split, as a stratum of malleable iron of greater or less thickness is thus produced on their surface. This conversion might probably be best effected in a reverberatory furnace with a sunken hearth, upon which the carbonate of soda would be fused. The consumption of carbonate of soda is inconsiderable, when the operation is properly carried on. Pure carbonate of soda must, however, be employed; or if the ordinary salt is to be used, it must first be ignited with charcoal, in order to convert all the sulphate of soda contained in it into sulphuret of sodium, for alkaline sulphates violently attack iron at a strong heat, and it is principally to this action that the rapid destruction of the iron stirring-rod used in the manufacture of sodium must be ascribed.– *Technologiste*, July 1857, p. 513; *Polytechn. Centralbl.* 1857, p. 1255.

PROCEEDINGS OF SOCIETIES.

Literary and Philosophical Society of Manchester.

October 6, 1857. (Dr. Joule in the Chair.)

"On a Yellow Colouring Matter obtained from the Leaves of the *Polygonum Fagopyrum*, or common Buckwheat." By Dr. Schunck.

It has been stated that the *Polygonum Fagopyrum* yields by fermentation indigo-blue. The author was unable to obtain a trace of that colouring matter from the plant, but on examination it was found to afford a yellow colouring matter in rather considerable quantity. This colouring matter crystallizes in small primrose-yellow needles. It is very little soluble in cold water, but soluble in boiling water, and still more soluble in alcohol. It dissolves easily in caustic alkalies, forming solutions of a deep yellow colour, from which it is again deposited in crystalline needles on adding an excess of acid. Muriatic and sulphuric acid change its colour to a deep orange, the colour disappearing on the addition of a large quantity of water. It is not decomposed when exposed for a length of time to the action of boiling dilute sulphuric acid, and is therefore not a copulated compound, like so many of the other colouring matters. Boiling nitric acid converts it into oxalic acid. It is also decomposed when its solution in alkali is exposed for some time to the air, being converted into an amorphous substance easily soluble in water, which resembles gum in appearance. The compound with oxide of lead has a bright yellow colour similar to that of chromate of lead. The watery solution imparts to printed calico, colours, some of which exhibit considerable liveliness. The composition of the substance is expressed by the formula $C^{3}\,H^{2}\,O^{2}$. The true formula is probably $C^{30}\,H^{20}\,O^{20}$. It appears to be identical with *Rutine*, the yellow colouring matter contained in the *Ruta graveolens*, or com-

mon rue, and in capers, and with *Ilixanthine*, a substance derived from the leaves of the common holly. The author obtained from 1000 parts of fresh buckwheat leaves a little more than 1 part of crystallized rutine. As the seed of the plant is the only part at present employed, it might be of advantage to collect and dry the leaves to be used as a dyeing material.

October 20, 1857. (W. Fairbairn, F.R.S. &c., President, in the Chair.)

"On some Applications of the Chromates of Potash in Metrical Analysis." By Mr. R. W. Pearson.

The object of the communication was—First, to place on a surer basis modes of estimating lead and baryta by metrical analysis. Secondly, to suggest some new applications of the principles involved, for the indirect determination of other substances. And lastly, to describe a process whereby chromium in its compounds may be metrically estimated. The manipulative part may be learnt by reference to a paper by the author, "On the Determination of Bismuth," in the Philosophical Magazine for March, 1856. The first section related to the determination of lead. After a critical examination of the methods now in vogue, the author gave a decided preference, both for celerity and accuracy, to the method based upon the use of bichromate of potash. For metrical analysis, lead salts may be divided into two classes, according to the nature of their solution.

If clear and transparent, the estimation is exceedingly simple, the result being known by the precipitate and the colour of the supernatant fluid. In coloured liquids, the formation of a yellow colour is partially or altogether concealed. In this case, sulphide of sodium paper is used as a secondary guide. The experimental results gave the mean error, in colourless liquids, as 0·0026 gr. of oxide of lead; while in dark liquids, the average error equalled 0·0042 gr. of oxide of lead.

The second section treated of baryta. This is effected in like manner, but by the aid of neutral chromate of potash. The mean error was 0·0024 gr. of baryta.

The third section discussed the estimation of combined sulphuric acid, by the double use of chloride of barium or other salt of baryta and chromate of potash. An excess of the former is added, and the surplus ascertained by fractional addition of the latter salt. Mean error 0·0022 gr. sulphuric acid. A salt of lead may be similarly used.

The fourth section was devoted to the consideration of sulphuretted hydrogen. The estimation of this compound in ores, waters, &c. the author finds may be made with great nicety by use of solutions of lead and bichromate of potash. A similar plan may be adopted with regard to carbonic acid, and this was detailed under the fifth heading. Collective allusion was also made to a numerous series of compounds, which give rise to insoluble bases with oxides of barium and lead. Such bodies may often be estimated advantageously by application of the general method given.

By modifying the above processes, metrical separations of sul-

phuric acid and sulphurous acid, of sulphuric acid and hydrochloric acid, of sulphuric acid and sulphurous acid from carbonic acid, and the latter from sulphuretted hydrogen, can be accomplished.

The concluding section embraced the use of lead or baryta solutions for the determination of chromic acid. The process is applicable to the oxide of chromium, which must be converted into chromic acid.

By so doing, oxide of chromium may be metrically separated from alumina and other oxides, and also from chromic acid.

The preparation of the various metrical test solutions was described, and to facilitate the same, the solubility of the salts used, and the specific gravity of their solutions had been determined anew, and the results tabulated. A peculiar gradation of test liquids was recommended for indirect estimations.

A colour-error unit analogous to the error of the meniscus in gas analysis was stated, and its corrective use explained.

The author, while regarding the processes described as well adapted for chemical research, also believes them capable of imparting greater precision to several industrial operations, and affording a safe and ready test as to the value of many commercial products.

December 1, 1857. (W. Fairbairn, F.R.S. &c., President, in the Chair.)

"On the Derivation and Composition of Rosolic Acid." By R. A. Smith, Ph.D., F.R.S.

Runge had found in the carbolic acid from tar, a substance which he describes as being of an orange colour, and as giving a beautiful rose colour to lime. He says, also, that it is capable of forming lakes, and combining with mordants so as to form a beautiful dye surpassing safflower, cochineal, and madder. Dr. Smith had found a similar colour from gas-liquor, and Mr. McDougall had found a large quantity of the lime compound when operating with carbolic acid. Dr. Smith showed that in a purified state it formed a dark-coloured resin unlike Runge's substance, and that it was formed in various ways with great ease by the oxidation of carbolic acid, and that it was a product of oxidation of that acid with the formula $C^{12} H^6 O^3$ or $C^{24} H^{12} O^6$. It formed picric acid by the action of nitric acid. It did not, however, form such compounds with the bases as Runge's acid, the colour of the compounds being destroyed as soon as the excess of base was removed; and in most cases the acid was easily separated from the base by means of ammonia.

The carbonic acid of the air readily destroyed the bright colour of the salts, and reproduced the dark brown colour of the acid itself. The colour, therefore, could neither be transferred to mordants nor to fabrics. For the same reason it could not serve as a pigment. In all probability, however, it was the same substance as found by Runge, although probably from not knowing how to prepare it in sufficient quantities he had not observed these facts. Although interesting, therefore, from a scientific point of view, any hope long entertained of applying the acid on the proposed plan in the arts was destroyed.

THE CHEMICAL GAZETTE.

No. CCCLXVI.—January 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the so-called Lactic Fermentation. *By* L. PASTEUR.

THE conditions of the production of lactic acid are well known to chemists. It is sufficient to add chalk to solution of sugar, and then a nitrogenous matter, such as caseum, gluten, animal membrane, &c., to cause the conversion of the sugar into lactic acid. But the explanation of the phænomena is very difficult; the mode of action of the nitrogenous plastic matter is unknown. Its weight is not sensibly changed, and it does not become putrid. It is modified, nevertheless, and is continually in a state of evident alteration, although it would be difficult to say in what this consists.

Minute researches have failed to discover the development of organized creatures in these operations. Where such have been observed, their presence was proved to be accidental and injurious.

The facts, therefore, appear to be favourable to the views of Liebig, who regards the ferment as an excessively alterable substance, which becomes decomposed, and excites fermentation in consequence of its own alteration. This, according to Liebig, is the first cause of all fermentations, and the origin of most contagious diseases. This opinion is supported recently by Fremy and Boutron, Gerhardt and Berthelot. They all reject the notion of any organized or vital influence in fermentation.

The author is of a different opinion. In the first part of this memoir he proposes to prove that just as there is an alcoholic ferment (yeast) which occurs wherever sugar is decomposed into alcohol and carbonic acid, there also exists a peculiar lactic ferment, which is always present when sugar is converted into lactic acid; if any plastic, nitrogenous matter may serve this purpose, this is because it is a suitable aliment for the development of this ferment.

Sometimes in ordinary lactic fermentations, above the deposit of chalk and nitrogenous matter, portions of a gray substance may be observed, in some cases forming a zone on the surface of the deposit. Under the microscope it cannot be distinguished from disaggregated caseum, gluten, &c., so that nothing indicates it to be a peculiar matter, or that it originated during the fermentation. Nevertheless this substance plays the principal part.

To isolate it in a pure state, the author extracts the soluble part of yeast by boiling it for some time with fifteen to twenty times its weight of water. The liquid is carefully filtered, and 50 grms. of sugar per litre are dissolved in it; chalk is added, and a trace of the gray matter just referred to is put in. The next day a brisk and regular fermentation is exhibited. The limpid liquid becomes turbid, the chalk disappears by degrees, at the same time that a deposit is formed, and gradually increased in proportion as the chalk is dissolved. All the well-known characters of lactic fermentation are observed. The extract of yeast may be replaced in this experiment by the decoction of any plastic nitrogenous body, fresh or altered according to circumstances.

The characters of this substance, the production of which is correlative with the phænomena of *lactic fermentation*, are as follow. Its appearance resembles that of yeast when examined in mass, and drained or pressed. Under the microscope it consists of small globules, or very short joints, either isolated or aggregated to form irregular flakes. The globules, which are much smaller than those of yeast, are strongly agitated by the Brownian movement. When washed by decantation with much water, and then suspended in solution of sugar, it acidifies the latter directly and progressively, but very slowly, because acidity greatly limits its action upon sugar. With chalk, which maintains the neutrality of the solution, the conversion of the sugar is greatly facilitated; even in operating with a very small quantity of material, the evolution of gas is manifest in less than an hour, and the liquid becomes charged with lactate and butyrate of lime. A very small quantity of this ferment is required for the conversion of a large amount of sugar. These fermentations should be effected without access of air, otherwise they are hindered by parasitic vegetations or infusoria.

Lactic fermentation, as well as ordinary alcoholic fermentation, is therefore an action correlative with the production of a nitrogenous matter which has all the appearance of an organized mycodermic body, probably very nearly allied to yeast. But the difficulties of the subject are not more than half got over. Lactic acid is certainly the principal product of the fermentation to which it gives its name, but not the only one. It is always accompanied by butyric acid, alcohol, mannite, and viscous matter, and the proportion of these varies most capriciously. There is a mysterious circumstance connected with mannite. Not only is the proportion formed subject to the greatest variations, but M. Berthelot has just shown, that if mannite be substituted for sugar in lactic fermentation, all other conditions remaining the same, the results of the fermentation are alcohol, and lactic and butyric acids. How then can there be a formation of mannite in lactic fermentation, since it might be supposed it would be destroyed as fast as it is produced?

The new ferment, washed and placed in pure solution of sugar, gradually acidifies the latter. The conversion of the sugar in this case becomes more and more difficult, in proportion as the liquid becomes more acid. When the acids have been saturated by chalk,

and the excess of sugar subsequently destroyed by yeast, the evaporated liquid contains mannite and viscous matter in variable proportions. Thus washed, lactic ferment in presence of sugar converts it into various products, amongst which there is always mannite, but this is on condition that the liquid always remains acid; for if the same experiment be exactly repeated with the addition of a little chalk, neither mannite nor gum is produced; if produced, they cannot persist, because the conditions of their own transformation are fulfilled.

When mannite is substituted for sugar in lactic fermentation, this substance ferments. It is easy to prove that in the numerous cases of the fermentation of mannite, it is the lactic ferment that is originated and produces the phænomenon. On mixing a solution of pure mannite with powdered chalk and fresh washed lactic ferment, the evolution of gas and the chemical transformation of the mannite will commence in an hour. Carbonic acid and hydrogen are produced; the liquid contains alcohol, lactic acid, and butyric acid, all the products of the fermentation of mannite.

Experiment proves that the lactic ferment acts directly upon lactate of lime, furnishing carbonate and butyrate of lime. But the action is first of all exerted upon sugar; and as long as there is any of this in the liquid, the ferment will act upon it in preference to the lactic acid.—*Comptes Rendus*, Nov. 30, 1857, p. 913.

On some new Compounds of Silicium.
By H. Buff *and* F. Wöhler.

1. *Siliciuretted Hydrogen Gas.*—This compound, which is remarkable from the property of igniting spontaneously in the air, is produced when a powerful electrical current is passed into a solution of chloride of sodium, through a positive pole of aluminium containing silicium. Its quantitative composition is not yet ascertained, as it has not been obtained pure and free from intermixed hydrogen gas. It appears to be certain, however, that the hydrogen gas, combined with silicium, undergoes a condensation. Its formation, and the paradoxical circumstance that in this case only hydrogen gas escapes at both poles, is due to the simultaneous production of chloride of aluminium and alumina at the positive pole; the latter combines with the former to constitute a basic salt which remains in solution. When aluminium containing silicium is employed as the negative pole, no siliciuretted hydrogen gas is produced. On the other hand, it is formed during the solution of such aluminium in muriatic acid, although then it is always mixed with so much free hydrogen that it is no longer spontaneously inflammable. When brought into contact with air, siliciuretted hydrogen gas is immediately inflamed, and burns with a white flame and with formation of fumes of white silicic acid. When a cold surface is held to the flame, it becomes coated with brown amorphous silicium. If the gas be passed through a red-hot glass tube, it is decomposed, and the walls of the glass become coated with brown

silicium. With chlorine gas it detonates as violently as with oxygen.

2. *Protochloride of Silicium and Hydrochloric Acid*, Si^2Cl^3+2HCl, is produced when silicium is heated not quite to perceptible redness in a current of dry muriatic acid gas. The hydrogen gas thus set free takes up no silicium. The compound is a colourless, very mobile liquid, which fumes strongly in the air, boils at 80°·6 F., and has a specific gravity of 1·5. With water it is immediately decomposed into muriatic acid and white silica. Its vapour is as inflammable as that of æther, and when mixed with oxygen gas and ignited by the electric spark, it ignites with a violent explosion, and with formation of silicic acid, perchloride of silicium, and muriatic acid gas. When passed in the form of vapour through a red-hot tube, it becomes decomposed into amorphous silicium, perchloride of silicium and muriatic acid. When passed over fusing aluminium, it disengages free hydrogen gas.

3. *Protobromide of Silicium and Hydrobromic Acid*, Si^2Br^3+2HBr, is produced in the same way as the protochloride. It is very similar to this, and constitutes a strongly fuming fluid, decomposable by water.

4. *Protiodide of Silicium and Hydriodic Acid*, Si^2I^3+2HI, is a dark red, crystalline, solid body, readily fusible and volatile. It fumes in the air, and becomes first of all cinnabar-red and finally snow-white; in water it is decomposed in the same way as the other compounds, but more slowly. From sulphuret of carbon, in which it dissolves abundantly with a blood-red colour, it may be obtained crystallized.

5. *Hydrated Oxide of Silicium*, Si^2O^3+2HO.—This is produced by the decomposition of the preceding compounds with water. It is obtained in abundance as a subsidiary product in the preparation of the protochloride, when the hydrogen gas saturated with the protochloride and the excess of muriatic acid gas escaping from the condensing vessel cooled below 32° F. is passed into water, which is kept strongly refrigerated. It is a snow-white amorphous body, essentially different in its appearance from the silicic acid separated from its compounds. It is very light and floats upon water. It sinks in æther. By both caustic alkalies and alkaline carbonates, and even by ammonia, it is dissolved with an effervescence of hydrogen gas forming an alkaline silicate; acids, even concentrated nitric acid, have no action upon it; it is dissolved only by hydrochloric acid with a brisk evolution of hydrogen gas. It may be heated to 572° F. without change, but above this point it ignites and smoulders away briskly, and with a phosphorescent light, whilst at the same time hydrogen gas is evolved, and ignites with explosion. When heated in oxygen gas it burns brilliantly. When heated in a covered crucible it does not remain white, but is coloured brown by amorphous silicium. It was proved by experiment, that when heated without access of air or hydrogen it really evolves siliciuretted hydrogen gas, but only at a temperature at which the greater part of the latter is again decomposed into hydrogen and brown silicium.

Hydrated oxide of silicium is somewhat soluble in water. This solution, however, is constantly undergoing decomposition with evolution of hydrogen gas. When freshly prepared it has a powerful reducing action; from perchloride of gold, for example, it immediately reduces metallic gold, from protochloride of palladium, black palladium, from selenious acid, red selenium, and from tellurous acid, gray tellurium. When nitrate of silver is poured upon it, the oxide immediately becomes pale brown; if ammonia be added, it becomes converted into black protosilicate of silver.

The authors state that in most of their analyses the amount of silicium was found more than ½ per cent. too high, whilst the possible sources of error must rather have given it too low, and that they have even analysed specimens of oxide the amount of silicium in which was found more than 2 per cent. higher than corresponds with the above formula, which must express the true constitution, as it is in accordance with that of the protochloride from which the oxide is produced. These oxides were also remarkably characterized by the fact that they burnt more vividly, and indeed with a red flame, and that even with free access of air they did not furnish a white silicic acid, but one coloured more or less brown by unignited silicium, so that, before analysis, they required to be converted into silicic acid by ammonia. From these and other circumstances, the authors regard it as most probable that there must be an oxide which is richer in silicium and consequently also a lower chloride corresponding with this, and that this is produced under certain conditions, and is frequently intermixed with the other. All their endeavours to arrive at positive certainty upon this point and obtain products of constant composition, and in agreement with probable formulæ, have hitherto been unsuccessful. However, as soon as they can again obtain silicium, the authors will continue these investigations, especially as they hope thereby to settle the question whether silicic acid is SiO^3 or SiO^2. It need only be mentioned, that they had specimens of oxide of silicium the composition of which very nearly corresponded with the formula $SiO + Si^2O^3 + 3HO$, and on one occasion, apparently in connexion therewith, a less volatile protochloride which had the remarkable property of igniting spontaneously when heated to boiling, burning with a red, sparkling flame, and depositing a large quantity of amorphous silicium.—*Nachrichten von der G. A. Univ. und der Königl. Gesellsch. der Wiss. zu Göttingen am* 12. *October* 1857.

On Phloretic Acid. *By* Professor H. Hlasiwetz.

[Concluded from page 12.]

A. *Binitrophloretic Acid*, $C^{18}H^7(NO^4)^2O^5$, HO.—Concentrated nitric acid acts violently upon phloretic acid. When the nitric acid is poured upon the phloretic acid, red fumes are immediately evolved, and the acid dissolves into a red fluid with frothing and evolution of heat.

After cooling, this becomes filled with yellow granular crystals. The quantity of nitric acid necessary for the decomposition is small, but there is a loss of the new product if the action be not moderated by refrigeration; otherwise the formation of oxalic acid cannot be avoided.

The crystals are yellow; they were freed from adherent acid, first upon a porous stone, and then by washing with cold water, and afterwards recrystallized from hot water, and finally from alcohol. Cold water dissolves very little of them, but even small quantities give it a fine yellow colour. Hot water dissolves the substance completely, and on cooling it again forms shining crystals very rapidly. Alcohol dissolves it more abundantly than water, and from this it is obtained again in prisms. Its colour is light citron-yellow. Alkalies dissolve it very readily, and the solution is intensely yellowish-red. The crystals fuse upon platinum, and burn with a sooty flame without residue. They do not deflagrate. When heated in a tube, they furnish an oleaginous brown distillate and a yellow smoke. Their taste is at first scarcely appreciable, but afterwards slightly bitter. They colour organic substances as intensely as picric acid, and undergo no loss of weight at 212° F. Analysis:—

C	41·84	42·00	18 =	108	42·18
H	3·56	3·35	6	6	3·12
N	10·69	11·20	2	28	10·93
O	..	..	14	112	43·77

The salts of binitrophloretic acid may be obtained by saturating the aqueous solution of the acid with the carbonates of the bases, or by decomposing concentrated solutions of the ammoniacal salt of the acid, and of a salt of the base to be combined with it. They deflagrate when heated.

The Potash-salt, $C^{18}H^6(NO^4)^2O^4, 2KO$, crystallizes in deep orange-red prisms. It is best recrystallized from dilute alcohol, in which it is less soluble than in water. During the spontaneous evaporation of a solution the efflorescences acquire a strong red colour, and reflect the light green.

It was dried at 248° F., and in order to avoid deflagration during the determination of the potash, it was moistened with an alcoholic solution of sulphuric acid. Analysis:—

	Calculated.	Found.	
$C^{18}H^6(NO^4)^2O^4$	71·68	..	..
KO	28·32	28·00	28·18

Baryta-salt, $C^{18}H^6(NO^4)^2O^4, 2BaO$.—Obtained by saturating the hot solution of the acid with carbonate of baryta; or more conveniently by mixing a saturated solution of chloride of barium with a solution of the acid neutralized with ammonia.

It is difficult of solution in cold water, and forms orange-yellow needles. It was observed that the salt, which was yellow at first, acquired a bright red colour by long keeping. The determination of the baryta was effected in the same way as that of the potash in the preceding salt. Dried at 248° F.

	Calculated.	Found.	
$C^{18}H^6(NO^4)^8O^4$	60·86	..	..
BaO	39·14	38·28	38·39

The Lime-salt, prepared in the same way as the baryta-salt, forms yellow needles.

The Lead-salt, obtained with acetate of lead and the ammoniacal salt, is a bright red precipitate. Examined with the microscope, it consists of granules arranged in lines.

The Silver-salt is a red precipitate, which becomes crystalline by standing.

The Copper-salt is a yellow precipitate.

Mercurial Salt.—With the ammoniacal solution of the acid, solution of bichloride of mercury gives a chrome-yellow precipitate, which is at first amorphous, but rapidly becomes crystalline; an excess of bichloride of mercury deprives the precipitate of colour, and causes its disappearance.

Acetate of zinc and the solution of the ammoniacal salt give an amorphous precipitate of a fine yellow colour.

Protochloride of tin gives at first a yellow precipitate, and then decolorizes the solution.

Perchloride of iron furnishes light brown flakes with a solution of the acid.

B. *Binitrophloretic Acid*, $C^{18}H^8N^2O^{14}$.—If phloretic acid be dissolved in water and nitric acid be dropped into the hot solution, an effervescence takes place, and hyponitric acid is evolved. At the same time the fluid becomes coloured, and brown resinous drops separate from it. If the heat be continued with the addition of a little nitric acid, the resinous drops gradually disappear, and in a short time the fluid becomes filled with yellow crystals. They have the same degree of solubility as binitrophloretic acid, but they do not appear, like this, in the form of light yellow prisms, but (especially when crystallized from alcohol) as dark, golden-yellow laminæ and scales of strong lustre and great beauty. This compound, so different in its external appearance, has nevertheless the same composition as the preceding, and may be regarded as isomeric with it. When dried at 212° F. its analyses gave

C	42·68	42·63
H	3·18	3·56
N	10·91	10·91

The alkaline and earthy salts of this acid show an unmistakeable difference in their degree of solubility from those of A. The solution of the ammoniacal salt of A is immediately thrown down in a crystalline form by chloride of barium and chloride of calcium. The salts of B with these bases can only be obtained by saturating the acid with the hydrates of the bases or their carbonates. The solution of the ammoniacal salt gives with sulphate of copper, a yellow, with nitrate of silver, a red, with acetate of lead, a red, with acetate of zinc, an orange, and with protochloride of mercury, a reddish precipitate. Most of these precipitates become crystalline by standing.

The Ammoniacal Salt, $C^{18}H^{6}(NO^{4})^{2}O^{4}, 2NH^{4}O$, obtained by evaporating the solution of the acid saturated with ammonia under the air-pump, effloresces in dark yellow needles.

	Calculated.	Found.
H	4·89	5·06
N	19·50	18·29

The Baryta-salt, $C^{18}H^{6}(NO^{4})^{2}O^{4}, 2BaO$, forms orange-yellow crystals united in warts. It becomes red when dried, deflagrates when heated.

	Calculated.	Found.
$C^{18}H^{6}(NO^{4})^{2}O^{4}$	60·86	..
2BaO	39·14	38·36

It appears that there exists between these two isomeric nitro-acids a relation analogous to that between nitrosalicylic and anilotic acids, which are also produced from one and the same acid under altered conditions.

Mononitrated phloretic acid could not be prepared.

Bibromophloretic Acid, $C^{18}H^{7}Br^{2}O^{5}, HO$.—For the preparation of this compound pulverized phloretic acid was put into a capsule, and bromine dropped upon it as long as any action took place. A violent reaction ensued, and hydrobromic acid was abundantly evolved; the mass was repeatedly triturated, and bromine added to it in small quantities.

The mass, which was at first doughy, soon became solid again; it was carefully mixed, and the excess of bromine was then allowed to evaporate at the ordinary temperature. After the volatilization of the bromine a slightly coloured powder remained. This was repeatedly washed with cold water, then dried over lime, and finally crystallized from alcohol. In this way colourless, hard, prismatic crystals were obtained.

An alcoholic solution may be frequently evaporated under the air-pump, to the consistence of a syrup, without the occurrence of crystallization. If the capsule be then taken out, one or more crystals with a funnel-shaped depression are suddenly formed in the mass, and soon afterwards the whole fluid solidifies into a hard mass. For complete purification, the acid was dissolved in hot dilute alcohol, precipitated by muriatic acid, and recrystallized from alcohol.

Bibromophloretic acid is insoluble in water, but readily soluble in alcohol and æther. It fuses very easily. Analysis:—

	Found.			Calculated.
C	33·49	18	=108	33·33
H	2·80	8	8	2·46
Br	49·20	2	160	49·03
O	..	6	48	15·08

The Ammoniacal Salt is produced by saturating the acid with ammonia whilst hot. It separates on cooling in short, colourless needles. A cold alcoholic solution of the acid, when mixed with ammonia, immediately gives a crystalline paste of this salt when

heated. It is sparingly soluble in cold water, and loses ammonia even at a gentle heat.

Baryta-salt.—When a solution of the ammoniacal salt is mixed with chloride of barium, an abundant separation of prismatic crystals of this salt quickly takes place. When dried at 248° F. its analysis gave,—

	Calculated.	Found.
$C^{18} H^{7} Br^{3} O^{5}$	80·41	..
BaO	19·49	19·61

Chlorophloretic Acid.—If powdered phloretic acid be put into a flask filled with chlorine gas, it melts with evolution of heat, the colour of the chlorine disappears gradually, and its place is taken by muriatic acid. The product is insoluble in water, but soluble in alcohol and æther. The solution exhibits no tendency to crystallize. After evaporation a sticky white mass remains. The soda-salt long retains the same consistency, but at length solidifies into a deliquescent crystalline mass.

Phloretylamic Acid, $C^{18} H^{11} NO^{4}$.—This was obtained by decomposing phloretic æther with strong ammonia. The æther was prepared from phloretate of silver with iodide of æthyle. In the presence of a little alcohol, the decomposition takes place very rapidly at a boiling heat. It was filtered away from the iodide of silver, and distilled in order to get rid of the excess of iodide of æthyle. The residue of the distillation was left standing with very strong ammonia in a closed bottle, and frequently shaken. In a few weeks the æther had entirely disappeared, and a small quantity of small shining crystals had separated. At this point the fluid solidified in a crystalline form after the alcohol and ammonia had been driven off.

On recrystallization from hot water (cold water dissolves very little of it), short, fine, shining prisms are formed. They dissolve in alcohol and æther, fuse between 230° and 239° F., and solidify in a crystalline form. When heated in a glass tube, they are partially sublimed, and when further heated evolve much ammonia. With perchloride of iron, the aqueous solution strikes a blue colour Analysis;—

C	65·75	18	= 108	65·46
H	6·96	11	11	6·66
N	8·05	1	14	8·48
O	..	4	32	19·40

According to the most recent investigations of Piria and Limpricht, this compound, which from its mode of production exactly agrees with the body hitherto regarded as salicyamide and which is homologous therewith, must have the formula $\left.\begin{matrix} C^{18} H^{8} O^{2} H, H, N, O \\ HO \end{matrix}\right\}$; that is, if the radical of phloretic acid be called phloretyle, phloretylamic acid, $C^{18} H^{8} O^{2}$, is equivalent to H^{2}. The acid nature of this body is, however, but slightly expressed. It does not decom-

pose carbonates, but nevertheless appears to form compounds with alkalies.

Perchloride of Phloretyle.—If perchloride of phosphorus and powdered phloretic acid be triturated together, the mass immediately becomes fluid, heated, effervesces, and evolves much muriatic acid. If the whole be then distilled, a certain quantity of oxychloride of phosphorus passes at 230° F., and the residue consists of a fuming liquid, which, when brought into contact with water, becomes decomposed principally into phloretic and muriatic acids. But phosphoric acid is also formed at the same time, so that the nature of this residue is complicated. Besides perchloride of phloretyle, it contains either a compound of anhydrous phloretic acid (oxide of phloretyle) with phosphoric acid, a view which Gerhardt has put forward with regard to perchloride of salicyle,

$$4(C^{18}H^{10}O^{6})+PCl^{5}=4HCl+C^{18}H^{9}O^{4},Cl+PO^{5}\left\{\begin{matrix}C^{18}H^{9}O^{5}\\C^{18}H^{9}O^{5},\\C^{18}H^{9}O^{5}\end{matrix}\right.$$

or, and this appears most correct, phloretic acid, being bibasic, has not the radical $C^{18}H^{9}O^{4}$, but $C^{18}H^{8}O^{2}$, and is to be written $C^{18}H^{8}O^{2}\left\{\begin{matrix}O,HO\\O,HO\end{matrix}\right\}$. Then the perchloride would not have the formula $\left.\begin{matrix}C^{18}H^{9}O^{4}\\Cl\end{matrix}\right\}$, any more than protochloride of salicyle is $\left.\begin{matrix}C^{14}H^{5}O^{4}\\Cl\end{matrix}\right\}$, but these chlorides are probably $C^{14}H^{4}O^{2}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$ and $C^{18}H^{8}O^{2}\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$ In this case the process might be expressed as follows:—

$$3(C^{18}H^{10}O^{6})+3PCl^{5}=3(C^{18}H^{8}O^{2},Cl^{2})+3HCl+2PCl^{3}O^{2}+PO^{5},3HO,$$

and then the occurrence of the oxychloride of phosphorus would also be explained. The mass in the retort cannot be heated to a higher temperature without being decomposed. It becomes brown, froths, and by continuing the temperature a further small quantity of oxychloride of phosphorus is obtained, whilst at last an inflated coal remains.

Phloretic acid and perchloride of acetyle act upon each other with evolution of muriatic acid, and a new acid is formed which exhibits an anomalous behaviour in many respects. Similar products are furnished by the perchlorides of butyryle and benzoyle. The author will return to these interesting compounds on another occasion.

After tracing so far the analogies between phloretic acid and the homologous salicylic acid (and anisic acid), it could not but be of importance to trace also the homologies in those products of decomposition which are formed in the salicyle and anisyle series by the distillation of the baryta-salts. By this process aromatic fluids of the formulæ $C^{12}H^{6}O^{2}\ldots$, $C^{14}H^{8}O^{2}$ are obtained. If therefore a compound could be prepared from phloretic acid homologous with

phenole and anisole, and isomeric with phænetole, this would furnish a very important piece of evidence in favour of the opinion which the author has endeavoured to establish in the foregoing. In point of fact, the body $C^{16}H^{10}O^2$ is produced in accordance with the equation

$$C^{18}H^{10}O^6+2BaO=C^{16}H^{10}O^2+2BaO,CO^2,$$

under the same conditions as phenole from salicylic acid. If phloretate of baryta be mixed with caustic lime (and a little powdered glass), and the mixture be submitted to dry distillation in small portions over the open fire, an oily distillate of a somewhat brown colour is obtained together with some water.

The water is drawn off, and the residue dried with chloride of calcium, and rectified. The product is colourless. On distilling it again with platinum wire in the vessel, the first bubbles were observed at 374° F. The portion passing at the commencement was separated from that which distilled over above 392° F.

The pure product is a colourless, strongly refractive oil, possessing a not unpleasant aromatic odour, resembling that of phenylic alcohol, and a burning taste. It irritates the skin, may be ignited when drawn up by a wick, and burns with a luminous, smoky flame. It is heavier than water, and but sparingly soluble therein. An experiment gave the spec. grav. at 53°·6 F.=1·0374.

In vessels containing air, it gradually becomes yellowish; single drops thicken, and acquire the pleasant odour of styrole. With alcohol and æther it mixes in all proportions. Chlorine, bromine, and nitric acid furnish products of substitution. It dissolves in sulphuric acid, and the solution, after standing for some time, is no longer precipitated by water. When saturated with baryta, and filtered, a solution of the readily decomposable baryta-salt of a conjugate sulphuric acid is obtained.

Albumen is coagulated by this compound almost as rapidly as by phenylic alcohol. When a chip of deal is drenched with the aqueous solution of the oil, and then with muriatic acid, and dried in the sun, a blue coloration is obtained as with carbolic acid. A check experiment with muriatic acid alone did not exhibit this phænomenon. At 0° F. the oil does not become solid, although very thick. The combustion was effected in a current of oxygen. Analysis:—

C	78·89	78·51	16=96	76·68
H	8·14	8·20	10 10	8·19
O	..	..	2 16	13·13

The vapour density was determined according to Natanson's modification of Gay-Lussac's method. The values obtained gave 4·23, supposing a condensation to 4 volumes.

A nitrated substitution-product of this compound is produced when it is dropped into strong nitric acid. The reaction is very violent; each drop as it falls hisses like red-hot metal in water, and large quantities are projected. After the compound had been dropped into the acid, the mixture was agitated until the disappear-

ance of the resinous drops which had separated; during this much hyponitric acid was evolved. After standing for several hours yellow crystals had formed; these were washed with cold water and recrystallized from alcohol. The small quantity of the substanee was insufficient for many experiments. It was employed for a determination of the nitrogen, which gave a result agreeing with the formula $C^{16}\,\frac{(NO^4)^3}{H^7}\,O^2$.

	Calculated.	Found.
N	16·34	16·56

A bromine substitution-product is formed still more easily than this nitrated body, by pouring bromine over the oil in a flat capsule until the cessation of the evolution of hydrobromic acid. After the small excess of bromine is evaporated, a white crystalline mass, soluble in alcohol, but insoluble in water, is obtained.

As regards the intimate constitution of the compound $C^{16}\,H^{10}\,O^2$, one might be tempted to bring it under the same point of view as anisole, which is produced under the same circumstances from anisic acid, homologous with phloretic acid according to the (empirical) formula. It is distinguished therefrom by containing an additional $C^2\,H^2$, whilst it is isomeric with phænetole.

Now anisole is $=\left.\begin{matrix}C^{12}H^5O\\C^{12}H^3O\end{matrix}\right\}$, that is phenylate of oxide of methyle, or more correctly oxide of phenylomethyle, a double æther which belongs to the class of compounds like æthylomethylic æther, &c., and which may actually be obtained by the same process as these (*Cahours*).

Thus regarded, $C^{16}\,H^{10}\,O^2$ would be $\left.\begin{matrix}C^{14}\,H^7\,O\\C^2\,H^3\,O\end{matrix}\right\}$ =oxide of toluenylomethyle.

Now if it be a law that homologous members of a series are most closely allied by the type of their constitution, this type also necessitates a similar behaviour, a typical process of decomposition. Wherever a number of compounds have been recognized with certainty as homologous, the mode of their formation and decomposition is the same, so that, for example, such a compound cannot furnish an alcohol as a product of decomposition under the same circumstances in which the following one gives an aldehyde, &c.

But we should be in this position, if we regard salicylic and anisic acids as homologous compounds in the strict sense, with phloretic acid as a third member of the series:—

$C^{14}\,H^6\,O^6$ salicylic acid,
$C^{16}\,H^8\,O^6$ anisic acid,
$C^{18}\,H^{10}\,O^6$ phloretic acid.

Salicylic acid, by decomposition with baryta, furnishes hydrated oxide of phenyle, an alcohol; but anisic acid gives anisole, a double æther. This fact is incompatible with a true homology of the corresponding compounds.

The boiling-point of phenylic alcohol is about 369° F. The law that the boiling-point should rise about 34°·2 F. with an advance of

$C^2 H^2$, requires that the boiling-point of anisole should be 397°·4 F. But it boils even at 369° F., and this also is a proof that phenylic alcohol and anisole cannot be homologous in the true sense. The true homologues of phenylic alcohol are benzoic alcohol which boils at 403° F., and the still unknown xylenylic alcohol, the theoretical boiling-point of which is 437° F.

If anisic acid possessed the same molecular constitution as salicylic acid, it would also necessarily be bibasic, whilst as yet we are only acquainted with its monobasic salts.

Anisic acid, when distilled in the form of its lime-salt with formiate of lime, furnishes anisylic aldehyde (*Piria*). Salicylic acid does not partake in this property.

A very great accordance, however, prevails in all these respects between salicylic and phloretic acids.—*Bericht der Akad. der Wiss. zu Wien*, xxiv. p. 237.

Synthesis of Wood-spirit. *By* M. Berthelot.

The alcohols may be prepared by fixing the elements of water upon hydrocarbons analogous to olefiant gas:—

$$C^4 H^4 + 2HO = C^4 H^6 O^2.$$

This fixation is effected by two processes; sometimes the carburet is combined with sulphuric acid, and the compound decomposed by water; sometimes it is first united with a hydracid so as to produce an æther:—

$$C^6 H^6 + HBr = C^6 H^7 Br.$$

By these processes we may obtain from hydrocarbons—

Vinic alcohol	$C^4 H^6 O^2$
Propylic alcohol.....	$C^6 H^8 O^2$
Amylic alcohol	$C^{10} H^{12} O^2$
Caprylic alcohol.....	$C^{16} H^{18} O^2$
Æthalic alcohol	$C^{32} H^{34} O^2$
.....	

in other words, ordinary alcohol and all the alcohols with a higher equivalent.

Only one, the simplest of all, methylic alcohol, or wood-spirit, $C^2 H^4 O^2$, could not be prepared in the same way. The author has effected the synthesis of this compound by means of marsh-gas. This synthesis rests upon the following reactions, which are easily foreseen, but difficult to realize from the gaseous nature of the substances operated on. By treating marsh-gas, $C^2 H^4$, with chlorine, we obtain, with other products of substitution, chlorhydromethylic æther, $C^2 H^3 Cl$:—

$$C^2 H^4 + 2Cl = C^2 H^3 Cl + HCl.$$

This æther, properly decomposed, fixes the elements of water, loses those of muriatic acid, and becomes converted into wood-spirit:—

$$C^2 H^3 Cl + 2HO - HCl = C^2 H^4 O^2.$$

I. During the action of chlorine upon marsh-gas various chemists have observed the formation of a gaseous compound containing chlorine; but this gas has never been analysed or accurately examined. Many authors have regarded it as presenting the composition of chlorhydromethylic æther, with which it would be, not identical, but only isomeric.

To obtain this compound, which forms his starting-point, the author mixes in equal volumes, in flasks of 1 litre capacity, 40 litres of chlorine and 40 litres of marsh-gas, purified by sulphuric acid, and collected over water; these flasks, closely stopped, are placed where they may receive irregularly reflected solar light. When the mixture is decolorized, the flasks are opened over mercury, and some fragments of potash are put into them with a few drops of water. The volume of gas is thus reduced nearly one-half; the remaining gas contains chlorhydromethylic æther, which must be isolated by a new series of operations, as, when thus prepared, it is far from pure; in the author's experiments it never formed more than one-third of the gaseous residue, the rest consisting of unaltered marsh-gas, and often of hydrogen. The preservation of this portion of marsh-gas is due to an irregular action of the chlorine; the chlorinated gas must therefore be isolated in order to determine its nature with certainty.

For this purpose the gaseous mixture is agitated with crystallizable acetic acid in the proportion of 250 grms. to 8 litres of the gaseous mixture; the gas is passed successively into flasks of 1 litre, reversed over the mercurial trough, and containing the solvent; the gaseous residue is then passed out into the atmosphere by means of a reversed siphon. The acetic acid, when boiled, evolves the greater part of the gas which it has dissolved; the rest may be extracted by saturating the acid with a very concentrated solution of soda. The gas is collected over mercury, and freed from vapours of acetic acid by agitation with fragments of moistened potash.

A gas is obtained which possesses a peculiar odour, and burns with a characteristic green flame and production of muriatic acid; it is soluble in $\frac{1}{4}$th of its volume of water, in $\frac{1}{35}$th of absolute alcohol, and in $\frac{1}{40}$th of crystallizable acetic acid; it is liquefiable at $-22°$ F., and, in a word, presents the same properties as chlorhydromethylic æther, of which it also possesses the composition, for 1 volume of gas, burnt in the eudiometer, furnished 1 volume of carbonic acid, evidently absorbing $1\frac{1}{2}$ volume of oxygen:—

$$C^2 H^3 Cl + O^6 = C^2 O^4 + 2HO + HCl.$$

The mercury is not sensibly acted upon during this combustion.

II. The identity of the compound obtained from marsh-gas with chlorhydromethylic æther being thus proved by analysis and by the study of its physical properties, it remained to check this by converting the compound into wood-spirit. This conversion was effected with the gas isolated by means of acetic acid, and with the crude gaseous mixture. The æther may be converted into wood-spirit by three processes:—

1. This æther, dissolved in acetic acid, and heated to 392° F. with acetate of soda, is converted into acetomethylic æther. This process is hardly applicable to any considerable quantities of material.

2. The æther heated to 212° F. for a week with an aqueous solution of potash, regenerates wood-spirit:—

$$C^2 H^3 Cl + KO + HO = C^2 H^4 O^2 + KCl.$$

With 2 litres of gas the author was able to isolate nearly 2 grms. of wood-spirit, but a considerable quantity of the latter is lost during the operation, in consequence of its volatility and the great surface of the vessels necessary for experiments with gaseous bodies. It is preferable therefore to form with the methylic alcohol a fixed compound, capable of isolation by the evaporation of its solution, and endowed with characteristic properties.

3. For this purpose the author employed the action of a mixture of concentrated sulphuric acid and sulphate of silver or mercury at 212° F. In this way methylosulphuric acid was formed. The simultaneous employment of sulphate of silver and sulphuric acid appears to be necessary, as neither of these reagents alone has any sensible action at 212° F. By this means methylosulphate of baryta is obtained in a crystallized and perfectly definite form. With this salt it is easy to prepare wood-spirit, methylobenzoic æther, or methyloxalic æther, which is characterised by its crystallization.

Thus marsh-gas, $C^2 H^4$, may be changed into methylic alcohol, $C^2 H^4 O^2$, just as olefiant gas, $C^4 H^4$, may be converted into ordinary alcohol, $C^4 H^5 O^2$, propylene, $C^6 H^6$, into propylic alcohol, $C^6 H^8 O^2$, &c. But these latter alcohols result from the hydratation of the carburets of hydrogen, whilst methylic alcohol, $C^2 H^4 O^2$, is produced by fixing oxygen upon marsh-gas, $C^2 H^4$, in accordance with an artifice analogous to that which connects allylic alcohol and its æthers with propylene, $C^6 H^6$. The author adds, that he produced the marsh-gas by means of its constituent elements—carbon and hydrogen.—*Comptes Rendus*, Nov. 30, 1857, p. 916

On the Chemical Constituents of the Brain. *By* Dr. W. Müller.

The brain of man contains a small quantity of creatine, as its nitrogenous constituent soluble in water.

The brain of the ox contains no creatine, but instead of this a body similar to leucine, and probably homologous therewith.

Volatile acids of the series $C^{2n} H^{2n} O^4$ occur in both brains.

Lactic acid is contained in both, in considerable quantities.

In the brain of the ox there is a small amount of uric acid, with a large quantity of inosite. Succinic acid, creatinine, urea, cystine, and taurine were not found in the brain.

If these results be compared with those obtained in the investigation of the muscular substance and glandular organs, first by Liebig and subsequently by Gorup-Besanez, Frerichs and Städeler, Cloetta, Virchow, &c., we find some differences. In the muscles it is found that the products of the decomposition of albuminous bodies consist

principally of creatine and creatinine. Leucine, tyrosine, and the allied bodies are wanting.

In the fluids of the glands, on the contrary, creatine and creatinine are wanting, whilst leucine and homologous bodies make their appearance.

In the brain leucine and creatine certainly appear, but both in such small quantity, that their occurrence here can only be of slight importance; they also appear as it were to displace each other in the two brains which have been examined for them. In proportion to these nitrogenous bodies, the brain contains a remarkably large quantity of hydrocarbons; these occurred in the fluid of the brain, but neither in that of the muscles, nor in that of the glands.

However, nitrogenous products of substitution are by no means wanting in the brain. They occur in the coagulum which is obtained when the brain, stirred up with water into an emulsion and mixed with solution of acetate of lead, is heated. From this, boiling alcohol extracts nitrogenous substances with cholesterine and oleic acid; the latter is separated from the nitrogenous bodies by æther. The author is still occupied with the investigation of these nitrogenous bodies (Couerbe's *cerebrot*, Fremy's *cerebric acid*).—Liebig's *Annalen*, ciii. p. 131.

New Fluid for the Blowpipe-Lamp. By F. Pisani.

The author recommends for this purpose a mixture of 6 vols. of alcohol of specific gravity 0·848 with 1 vol. of turpentine and a few drops of æther. Wood-spirit may be substituted for alcohol, and of this 4 vols. are sufficient. The liquid must be perfectly limpid, as otherwise the undissolved excess of turpentine will cause the lamp to smoke.

Of the calorific effect of this fluid the author gives the following examples. A platinum wire $\frac{2}{10}$ths of a millimetre in diameter was fused at the extremity by the ordinary blowpipe. An iron wire of $\frac{2}{10}$ths of a millimetre was also fused into a globule 2 millimetres in diameter. M. P. Schmidt fused 4·6 grs. of copper and 23·5 grs. of silver in a cavity in charcoal, and also performed cupellations with as much as 5 grms. of argentiferous lead.

On the average, with a little practice, 2 to 3 grms. of copper and 15 grms. of silver may be fused by it, and cupellations may be effected with 3 grms. of lead. Carbonate of soda is fused by it with as much ease as cyanide of potassium by the spirit-lamp. The reducing flame, which is recognized with difficulty with other combustibles, makes its appearance here very distinctly.—*Comptes Rendus*, Nov. 23, 1857, p. 903.

On some Products of Decomposition of Sebacate of Lime. By Dr. T. Petersen.

By the dry distillation of suberate of lime, Boussingault and Tilley obtained suberone and an aromatic oil which they regarded as benzole. Calvi observed that during the dry distillation of seba-

cate of lime there is a formation of aldehydes, especially propylic aldehyde.

By similar treatment of large quantities of sebacate of lime, the author has obtained,—1. propylic aldehyde; 2. œnanthal; 3. small quantities of benzole, besides a solid hydrocarbon, sebacine. These products, in connexion with sebacic acid from which they are produced, show relations of the sebacic acid series, $C^n H^{n-2} O^8$, with the fatty acids and benzoyle bodies. The sebacic acid was prepared from castor oil.

During the distillation of the salt, the above mentioned bodies pass in an oleaginous form. Towards the end the solid body distils over.

Sebacine, $C^{20} H^{18}$, is a hydrocarbon, which is readily dissolved by alcohol and æther. Concentrated sulphuric and nitric acids act upon it but slightly; this is the case also with caustic potash. With sulphuric acid it forms a red fluid, but on the addition of water a complete separation takes place; this behaviour may be employed for its purification. Sebacine is tasteless and inodorous, and lighter than water. It fuses at 131° F., and is volatilized at a temperature above 572° F. Analysis:—

C	86·70	20	86·9
H	13·28	18	13·1

Liebig's *Annalen*, ciii. p. 184.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new Method of obtaining Carbonate of Potash from Felspar and similar Minerals. By Dr. E. Meyer.

The author's process consists essentially in decomposing the mineral by calcination with lime, and then treating it with water under a pressure of 7 to 8 atmospheres. With felspar 14 to 19 equivs. of lime are used to 1 equiv. of felspar, or to 100 parts of felspar 139 to 188 parts of lime.

The lime is employed either as hydrate or in the form of chalk; it is intimately mixed with the felspar to a plastic mass, which is made into round balls of 3 to 4 inches in diameter, slowly dried, and then exposed to a temperature between a bright red and a white heat. The temperature must be so high, that the mass, after burning, may contain neither carbonate of lime nor uncombined caustic lime. It should therefore exhibit a very inconsiderable elevation of temperature with water. It is usually caked together. Of course, for such a decomposition a very intimate mixture of the felspar and lime is requisite. The more lime employed, the shorter the time necessary. After burning, the mass is powdered and heated with water in a vessel capable of bearing a pressure of 8 atmospheres, in which the decomposition is completed in 2 to 4 hours. The solu-

tion above the powder (which is never firmly solidified, as the formation of steam probably prevents cohesion) is caustic to the touch, is free from hydrate of lime, and always contains all the soda, and potash to the amount of about 9 to 11 per cent. of the weight of the felspar employed.

A second extraction of the powder freed from the solution of potash is of no great use; little potash, but plenty of lime is dissolved; the latter cannot be taken up by the solution in the first instance. It is of no great advantage to continue the extraction longer than 4 hours.

If the alkaline solution, after saturation with carbonic acid, be evaporated to dryness, a little alumina and silica separate first of all; the carbonate of soda then crystallizes, and at last carbonate of potash remains, which, when pure minerals are employed, is perfectly free from other acids.

As regards the mass remaining insoluble in water, the very intimate mixture of its constituents renders it peculiarly suitable for the preparation of a Portland cement, the composition of which varies within the same limits. These cements, however, sometimes contain more alumina. This want of alumina, if it be a defect at all, is easily supplied by the addition of a little clay, with which the residue need only be mixed. The author has found, however, that the powder taken out of the kettle, and again strongly calcined, sets very rapidly and firmly under water, so that the addition of clay is unnecessary.

As a matter of course this mode of preparation will not be applied exclusively to pure felspar, as other felspars or minerals containing potash, must also be adapted for this purpose. Thus, for example, there are many granites which contain about 7 per cent. of potash, and from which the manufacture of potash would appear to be remunerative. Of course, in this case, the chemical composition is to be taken into consideration, and the amount of lime added to be modified accordingly. All that has to be done is to establish the proportion of 3 or 4 equivs. of base to 1 equiv. of acid, in which potash, soda, lithia, lime, and magnesia are to be regarded as bases, and silica, alumina, and oxide of iron as acids. Any chlorine or fluorine that may exist has no influence, and magnesia, instead of being injurious, has been found to be preferable to lime for the separation of potash. Moreover, it is well known that mica, which would play an important part when granite is employed, is far more easily decomposed than felspar, for, as Mitscherlich has lately discovered, it is even completely decomposed by muriatic acid in a glass tube at 212° F.

The points to be observed in carrying out this process on a large scale are now to be referred to; these, however, may easily require modification by local and other circumstances.

As the abundant result in potash depends especially upon the complete decomposition of the felspar, and the latter can only be effected by a very intimate mixture with lime, the greatest attention is to be paid to the fine division of the substances to be employed,

in order that in the intermixture the portions of felspar may be in contact with the lime in many places. The felspar, or the mineral containing felspar (of course, only granites with a small proportion of quartz will be operated on), is burnt in a furnace which works uninterruptedly, or in any reverberatory furnace, taken out of the fire whilst still red-hot and thrown into water. By this treatment it will be split in every direction, and rendered sufficiently soft for further division. It is then powdered under stampers or between cast-iron crushing rollers, and afterwards ground with water upon mill-stones. The bottom stone and the runner must be of quartz or granite, and possess considerable weight. The finely ground powder is then passed through sieves into the lixiviating apparatus, very finely lixiviated, and conducted into pits to settle. It is of the greatest importance only to employ fine lixiviated powder in the manufacture, as this greatly facilitates and hastens the decomposition by ignition, and causes a saving in fuel. The time occupied in lixiviation is not so considerable as it might appear at the first glance, as the rule adopted in the porcelain factories is not to be applied here. The greater specific gravity of the felspar causes it to settle far more rapidly than clay; it is unnecessary, as in porcelain factories, to bestow great care on purity, on the exclusion of dust, iron, &c., so that the simplest arrangement is sufficient for the purpose. The coarser powder is, of course, ground again.

A similar fine division is required for the lime, and when this is employed in the burnt state, it is most completely effected by slaking. Nevertheless when circumstances admit of the employment of carbonate of lime, the latter is to be preferred, because the balls or cakes prepared with it shrink less in drying, and retain more cohesion and solidity in the fire. In this case, of course, lixiviation is necessary.

In any case the lime and felspar must be in a state of the finest division before they are mixed together. The author does not think it necessary to say anything about the proportionate weights beyond what has been already stated; it is impossible to give any definite numbers, as they would be different for each raw material, for which reason a preliminary analysis is necessary. So much lime must always be added, that 3 or 4 equivs. of base may be presented to 1 equiv. of acid. It is to be observed, however, that as the materials are obtained in the form of a fine mud, the amount of moisture in them must be determined, when the proper quantities may be arranged by measure upon this basis. Measuring in this way is more exact and convenient than weighing.

The intimate mixture of the materials is most conveniently effected by means of a clay-mill, the usefulness of which is now well known. The paste is allowed to pass through until it is perfectly homogeneous. As soon as this is the case, the mixture issuing from the clay-mill is cut by the machine itself into cylindrical pieces of 5 to 6 inches in length, and 2 to 2½ inches in diameter. These are slowly dried, and then put in the furnace to be burnt.

The best furnace for burning the mass is the porcelain furnace,

because a more uniform heat can be attained in all parts of it than in the ordinary tile-furnaces. The latter may, however, be employed. A blast-furnace with a permanent blast would also be suitable, although inequalities of temperature are very liable to occur in it in different parts. The porcelain furnaces may be 2 or 3 stages high, and be furnished with 4 or 6 charges. Any fuel may be used, as the ashes carried on by the draught cannot produce the same injury here as in the burning of porcelain. The necessary temperature is a bright red heat, but it should be ascertained for each material by some preliminary trial burnings, as the greater or less degree of fusibility plays an important part, and fusion is not necessary. The cylinders contract considerably by burning, and are partly broken up. They are ground, and then mixed with water in the steam-kettle, in which the decomposition is to take place.

For the sake of simplicity and easy management, several kettles are heated by the steam of one generator. It is then unnecessary to moderate the fire during the emptying of the kettles, but the refrigeration necessary for emptying and filling them may be produced by simply shutting off the steam. A double bottom is also unnecessary, as a solidification of the mass and consequent overheating of the wall of the kettle cannot take place. The powder is put into the kettle by a suitable arrangement; the necessary quantity of water is let in, and then the connexion with the steam-generator is established. Fluid may be drawn off by a cock, to ascertain the quantity of alkali dissolved. When the decomposition is completed, the solution is allowed to flow out into clearing vessels by the pressure of the steam. When the suspended pulverulent mass has settled, the supernatant lye is conducted into the evaporating pans. The powder remaining in the kettle is cleaned out, and new masses immediately introduced, so that the working of the kettle is continued uninterruptedly. The lye, which contains caustic potash and soda, is either sold as such, or saturated with carbonic acid by passing the air of the fire over it, by which the evaporation is hastened at the same time. If the decomposition has been complete, no lime separates in this process, but only alumina and silica, which were dissolved in the caustic lime; this sediment is raked together and removed. During the subsequent cooling the carbonate of soda crystallizes, whilst the more soluble carbonate of potash is obtained by calcination. The carbonate of potash thus obtained is almost chemically pure, and far preferable to any prepared from the ashes of plants.

The powder taken out of the kettle and the clearing vessels, which may be again lixiviated to furnish a lye which may be employed afterwards instead of water, contains the constituents of a hydraulic cement. It is made into balls, or by means of a clay-mill into cylinders, either by itself, or with the addition of a little clay, and then burnt in a furnace. After burning, the pieces are pounded in the dry state, finely ground between granite rollers, and sifted; they then furnish a cement which resembles Portland cement in its composition, but far exceeds it in homogeneity.—Dingler's *Polytechn. Journ.* cxliii. p. 274.

THE CHEMICAL GAZETTE.

No. CCCLXVII.—February 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Equivalent of Manganese. *By* CARL VON HAUER.

FROM the attempts which have hitherto been made to establish the equivalent of manganese, and, indeed, from those which are regarded with the most confidence, we get the numbers 27·6 and 28 or 345 and 350, according as hydrogen is regarded as = 1 or oxygen as = 100.

The variations to which this number is subject consequently amount in the one case to 0·4 and in the other to 5. Both numbers are alternately adopted in our manuals and text-books.

Such an uncertain knowledge of the fundamental number of an elementary body, is quite sufficient to induce us to regard it as no longer satisfactory in the present state of science. But if it be of the highest importance in general to ascertain the equivalent numbers of the simple bodies as exactly as possible, in order to furnish an admissible starting-point for the numerous inferences which are founded directly upon them, this importance becomes still greater with a metal such as manganese. This is one of the very widely diffused substances, of which we know numerous compounds, both natural and artificial.

However, it is not to be expected that the present knowledge of the stochiometric nature of the numerous compounds of manganese would be influenced by a closer approximation to the knowledge of the true equivalent of that metal. Any such more exact knowledge would only be capable of enabling us to attain to a more precise agreement of the analyses of the compounds of manganese with their theoretical composition as evolved from the equivalent of manganese.

Without taking this into consideration, however, another question of peculiar interest is attached to the exact determination of the equivalent number of this metal. This is the question whether manganese has really the same equivalent as iron, which is so nearly allied to it, as appears to be the case from the experiments of some chemists, or whether it is different therefrom as shown by those of others.

As the equivalent of iron has been very exactly ascertained by the researches of Erdmann, Marchand, and Maumené, all that remains to be done for the settlement of the point in question, is to determine the equivalent of manganese by a greater number of experiments than have hitherto been made.

The first noteworthy attempts at the determination of the amount

of oxygen in the oxides of manganese are to be ascribed to John. A precise attempt to determine the equivalent was subsequently made by Berzelius. He dissolved metallic manganese in sulphuric acid, evaporated it to dryness, and calcined the salt slightly. In this way 0·5075 grm. of metal gave him 0·7225 grm. of an oxygen compound which he took to be the oxide of the composition $Mn^2 O^3$, as he was not aware that by this means proto-peroxide is produced. The latter grade of oxidation was only detected subsequently by Arfvedson. From this Berzelius calculated as the equivalent of manganese the number 355·79, in which, however, some error must have crept in, for the results described give 354·07 (28·32 if H=1).

If we suppose that in this experiment Berzelius actually obtained proto-peroxide of manganese, the equivalent of manganese obtained from this appears to be 27·76 with H=1.

According to Berzelius analyses of chloride of manganese and of protosulphate and protocarbonate of manganese were made by Davy and Forchhammer; these, however, may be passed over here, as well as some analyses of Berthier. Of more importance are the investigations of Arfvedson upon chloride of manganese, which he obtained by heating protocarbonate of manganese in a current of chlorine gas. Of this 1·508 grm. gave with nitrate of silver 3·408 grms. of chloride of silver. From this he calculates the composition of protoxide of manganese as follows:—

77·856 Mn
22·144 O.

According to the equivalents of silver (108·1) and chlorine (35·5) now adopted, his analysis leads to the equivalent number of manganese =350·53 (28·04 if H=1). But Arfvedson states that some oxide was mixed with his chloride of manganese.

Further investigations with the view of ascertaining the equivalent were made known by Turner. He decomposed the protocarbonate, protosulphate, and protochloride. In 100 parts of the carbonate he found—

56·853 MnO
34·720 CO^2
8·427 HO.

He ascertained the composition of the sulphate by determining the quantity of sulphuric acid which is taken up by weighed quantities of protoxide of manganese.

9·0 grs. protoxide of manganese gave 19·01 grs. of protosulphate.
4·855 „ „ „ „ 10·26 „ „

Lastly, by precipitation with nitrate of silver he obtained 28·42 grs. of chloride of silver from 12·47 grs. of protochloride of manganese.

From all these experiments Turner calculated the equivalent of manganese at 28·06 (350·75 if O=100).

If the results of Turner's analyses be calculated according to the equivalents now admitted, we obtain the following equivalent values for manganese:—

From $MnO\,CO^2$ 28·02
„ $MnO\,SO^3$ 27·94 } average 27·82 { 350·25 / 349·25 } average 347·75.
„ Mn Cl 27·50 { 343·75

The differences which had been obtained by Turner and Arfvedson in the analysis of chloride of manganese induced Berzelius to take up this investigation afresh.

I. 4·20775 grms. of chloride of manganese gave him 9·575 grms. of chloride of silver.

II. 3·063 grms. of chloride of manganese gave him 6·9691 grms. of chloride of silver.

From this Berzelius deduces as the most probable equivalent the number 345·9 (27·67).

If we regard silver as above =108·1 and chlorine =35·5, the equivalent of manganese calculated from these two analyses is—

	H=1.	O=100.
I.	Mn=27·60	345·0
II.	Mn=27·61	345·0

Lastly, Brandes also determined the equivalent of manganese by the analysis of the protochloride. From two analyses in which crystallized protochloride was decomposed in the ordinary analytical way, namely by precipitation with carbonate of potash and nitrate of silver, he deduced the equivalent of manganese =28·51 —28·54.

The various numbers which have been obtained by the analysis of the protochloride of manganese, and which certainly deserve the most consideration, as the determination of the chlorine is to be regarded as one of the best processes, are therefore as follows:—

	H=1.	O=100.
Arfvedson	28·04	350·5
Turner	27·50	343·75
Berzelius	27·60	345·0
	27·61	345·1
Brandes	28·51	356·45
	28·54	356·76

Arfvedson himself states that his protochloride of manganese contained some oxide. As, however, he only submitted 1·5 grm. to analysis, even a very small quantity of oxide must have shown the amount of chlorine notably too small, by which the equivalent of manganese must have proved too high. Turner prepared his protochloride with great care, depriving it of its water in an atmosphere of carbonic acid, by which the possibility of its oxidation was excluded. The two experiments of Berzelius agree very closely both with each other and with Turner's. Lastly, as regards the analysis by Brandes, the process therein adopted renders it probable that the amount of chlorine found may have been too small, and that of manganese too high, by which means the equivalent of manganese must also have been calculated too high.

All grounds of probability therefore are in favour of the numbers

27·5 and 27·61 of Turner and Berzelius, so that it appears almost unintelligible, how, notwithstanding this, the simple number 28 has repeatedly been adopted.

The author effected his determinations by reducing protosulphate of manganese in a current of sulphuretted hydrogen gas at a high temperature, and obtained the number 27·5 (343·75 if O=100), which, consequently, comes very near to these two statements.

For the preparation of the sulphate, he made use of a very pure and beautifully crystallized pyrolusite from Bohemia. The only impurities which it contained were traces of peroxide of iron, baryta, and a little quartz. From the latter it could not be entirely freed mechanically, as even the interior of the crystals contained small granules of quartz. There was consequently no particular difficulty in purifying it completely.

The finely-powdered substance was reduced in a current of hydrogen gas, dissolved in boiling sulphuric acid, and after long boiling, filtered from the insoluble residue consisting of quartz and a little sulphate of baryta. This solution was heated for a long time with the addition of a little nitric acid in order to convert the small quantity of iron into peroxide, and the protoxide of manganese was then precipitated by oxalic acid. The precipitate was washed with hot water, first by decantation and afterwards upon a filter until the washing-water on running away no longer had an acid reaction. The dried protoxalate of manganese was then converted into protoperoxide by calcination. This was again washed for a long time with hot water upon a filter, and then dissolved in muriatic acid with the addition of alcohol. This solution was precipitated by carbonate of ammonia; the precipitate was washed until no more chlorine was detectible in the filtrate, the carbonate was dissolved in dilute sulphuric acid, and the solution evaporated to crystallization. The crystals obtained were twice recrystallized. For this purpose the salt was each time deprived of water by heat, finely powdered, and exposed to a continued red heat; it was then dissolved in water and filtered. The last filtrate obtained was finally tested as to its purity; ferrocyanide of potassium and sulphocyanide of potassium gave no trace of a reaction for iron. A larger quantity of the fluid, precipitated by sulphuret of ammonium, and rapidly filtered, gave no reaction in the filtrate with oxalate of ammonia and phosphate of soda; nitrate of silver also gave no indication of the presence of a residue of chlorine in the original solution. As, moreover, litmus paper was not in the least reddened by the solution, it might be regarded as perfectly neutral and pure. It was evaporated to dryness in the water-bath, and then completely dried in a porcelain crucible in an air-bath at about 572° F.; it was then powdered and kept in a well-stopped bottle.

Some preliminary experiments proved that protosulphate of manganese cannot be entirely decomposed by the heat of a lamp, but that a higher temperature is necessary for that purpose. A porcelain reduction-tube was therefore substituted for the glass one; it was brought to a strong red heat in a Liebig's combustion furnace

with a charcoal fire. In other respects the arrangement of the apparatus remained the same, except that the gas was allowed to flow through under a somewhat stronger pressure. In this way a complete réduction was effected, for no trace of sulphuric acid could be detected in the sulphuret of manganese obtained.

The weighing of the protosulphate of manganese required rather more care, as this substance is somewhat more hygroscopic than sulphate of cadmium. With quantities of 4 to 7 grms., such as were used for the different experiments, the amount of water taken from the atmosphere was 1 to 3 milligrms. during the first weighing. Nevertheless, by the precautions already detailed, this source of error may be reduced to a minimum. The porcelain tray with the sulphate was repeatedly heated to about 500° F. in the air-bath, allowed to cool over sulphuric acid, and weighed; these operations were repeated until two consecutive weighings showed no differences. Almost without exception the third weighing agreed with the second, but when there was any differenee, it only amounted to a fraction of a milligramme. From this it follows that the salt is certainly somewhat hygroscopic, but not to such a degree as to lead to any fear that the result could be essentially injured by it. The metallic sulphuret obtained was always firmly caked together; it occupied scarcely half the volume of the sulphate. Here also care was taken to press the latter firmly into the porcelain tray, in order to prevent fine particles from being carried away by the gas flowing over it. At first it was always moderately heated by the application of a few pieces of charcoal, but at the conclusion it was brought to a strong red heat. The sulphuret of manganese obtained at this high temperature is of a dark green colour, and not in the least hygroscopic. If a quantity be left, even for a considerable time, upon the scale, no increase appears. The sulphuret obtained at a lower temperature is of a paler green, and resembles protoxide of manganese.

In all 11 reduction experiments were made, of which two were rejected and are not taken into the following calculation, as they differed widely from all the others here detailed. Nevertheless the errors which had occurred in these cases could not be satisfactorily ascertained, and they must be ascribed to some mechanical loss. The results of the other 9 experiments are as follows:—

Experiment.	Quantity of sulphate employed.	Sulphuret of manganese obtained.	Oxygen as loss of weight.	One part of protosulphate of manganese consequently contains
I.	4·0626	3·3425	1·7201	0·423398
II.	4·9367	2·8442	2·0925	0·423866
III.	5·2372	3·0192	2·2180	0·423508
IV.	7·0047	4·0347	2·9700	0·424001
V.	4·9157	2·8297	2·0860	0·424354
VI.	4·8546	2·7955	2·0591	0·424154
VII.	4·9978	2·7899	2·1179	0·423766
VIII.	4·6737	2·6934	1·9803	0·423771
IX.	4·7240	2·7197	2·0043	0·424280

From the equation

$$\mathrm{Mn}\,\frac{4\mathrm{BO}}{\mathrm{A}-\mathrm{B}}-\mathrm{S},$$

in which Mn represents the equivalent of manganese
O „ „ „ oxygen
S „ „ „ sulphur
A „ the quantity of the sulphate investigated, and
B „ „ of sulphuret of manganese obtained, the following values may be calculated:—

Experiment.	Calculated equiv. of manganese if O=8.	Difference from the number 27·5	Calculated equiv. of manganese if O=100.	Difference from the number 343·75.
I.	27·5788	+0·0788	344·635	+0·885
II.	27·4955	−0·0045	343·694	−0·056
III.	27·5592	+0·0592	344·480	+0·730
IV.	27·4715	−0·0285	343·394	−0·356
V.	27·4086	−0·0914	342·607	−1·143
VI.	27·4442	−0·0558	343·052	−0·648
VII.	27·5132	+0·0132	343·915	+0·165
VIII.	27·5231	+0·0231	344·039	+0·289
IX.	27·4218	−0·0782	342·772	−0·978
Average	27·4906	0·0480	343·632	0·6000

The average of these numbers is consequently so near the number 27·5, that it may probably be regarded as the correct one. It differs only by 0·1 from that at which Berzelius arrived by a very different course. For the present it may be a matter of indifference whether we take the equivalent of manganese as 27·5 or 27·6, but the author at all events believes that he has furnished the proof that the equivalent of manganese is certainly lower than that of iron, and that the number found by him can only be a very little removed from the truth.

Even before the author commenced the investigation just detailed, he had endeavoured to ascertain the equivalent of manganese by the reduction of its red oxide in hydrogen gas.

As has already been mentioned, there is a great inconvenience in the fact that the quantity of oxygen which the red oxide loses in this case is proportionally small. This source of error may certainly be avoided to a certain extent when great quantities, such as 30 to 40 grms., are reduced. For the preparation of the sulphate, the author had calcined a quantity of about half a pound of peroxide of manganese at once in hydrogen gas, and found that although the stratum was of considerable thickness, the reduction had taken place down to the bottom of the large tray. A portion of the protoxide obtained, when treated with muriatic acid, showed no evolution of chlorine. A reduction of large quantities of red oxide would therefore be quite practicable in this respect. But the author came upon another difficulty which he had not foreseen.

This consists in the fact that the red oxide obtained artificially is an extremely hygroscopic substance. This applies especially to

the product obtained by the ignition of the protoxalate or protocarbonate, the fine division of which may partly contribute to this result. The proto-per oxide obtained by the continued ignition of the protonitrate is more compact, and attracts moisture with rather less avidity, but still always much too rapidly to allow of its being weighed with any approach to exactitude.

A direct experiment made in this direction gave the following result:—

8·1 grms. of red oxide, moistened with nitric acid and strongly ignited, were left to cool over sulphuric acid. After cooling the crucible was weighed as quickly as possible, although for the reasons referred to, this is only approximatively possible; it is then weighed a quarter of an hour afterwards. In this short time the above quantity had increased about 19 milligrms. in weight.

As the usual mode of determining manganese in analyses consists in weighing the red oxide obtained by the ignition of the carbonate, this circumstance may give rise to considerable errors when it is not sufficiently taken into account.

In order to obtain from the direct relation of manganese to oxygen, some kind of proof for the number deduced from the reduction of the sulphate, the author endeavoured to convert weighed quantities of protoxide of manganese into sesquioxide, and this by ignition in contact with atmospheric air. The operation was effected in a platinum crucible, the cover of which closed it exactly. After the completion of the ignition the cover was applied, and the whole was allowed to cool over sulphuric acid and weighed; this operation was repeated until the weight exhibited no further change. The protoxide, as obtained by reduction with hydrogen gas at a strong red heat, proved to be but slightly hygroscopic, so that it is better adapted for weighing. To effect a complete oxidation, the powder was frequently stirred with a platinum spatula, which was weighed with the rest. Two experiments gave the following results:—

Experiment.	Protoxide of manganese employed.	Sesquioxide obtained.	Oxygen taken up for 100 parts.	Calculated equivalent. O=8.	Calculated equivalent. O=100.
I.	4·3808	4·710	7·5146	27·486	343·57
II.	8·3800	9·009	7·5059	27·527	344·08

The author does not lay any great weight upon these numbers, as he feels convinced that greater differences would probably occur if the experiments were repeated frequently, since every milligramme which is taken into calculation erroneously influences the first decimal of the equivalent, but they nevertheless serve to a certain extent for the confirmation of the previous results. Nor can it be doubted that by working very correctly and employing every precaution, as was done by the author in these two experiments, we might, by taking the average of many trials in this way, arrive at a certain conclusion as to the equivalent of manganese. This would be materially assisted by the employment of much larger quantities of protoxide.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxv. p. 124.

On some Compounds of Oxalic Acid with Metallic Oxides.
By A. Souchay *and* E. Lenssen.

Protoxalate of Mercury, $\left.\begin{matrix}Hg^2\\Hg^2\end{matrix}\right\}O^2, C^4O^6$.—Protonitrate of mercury is brought into contact with an excess of oxalic acid. A heavy precipitate consisting of small microscopic crystals is formed. It is insoluble in cold water, alcohol, and æther. Anhydrous. Contains 84·67 Hg (calculated 85·24).

When heated for a considerable time to 212° F., it is decomposed into mercury and peroxalate of mercury. At 275° F. it deflagrates. If it be quite free from hygroscopic water, a salt which is obtained when peroxalate of mercury is heated to 327° F., it bears a temperature of 347° F.

When protoxalate of mercury is boiled for a long time with water, it is decomposed into the persalt and mercury, and as the persalt is somewhat soluble in water, this behaviour may give rise to a mistaken notion that protoxalate of mercury is soluble in water. The protosalt is insoluble in oxalic acid and in cold nitric acid. It dissolves in hot nitric acid. It is insoluble in oxalate of potash, but when boiled, oxalate of mercury and potash is formed, whilst mercury is separated. It behaves in the same way with oxalates of ammonia and soda. Potash and soda separate black protoxide of mercury from it. Phosphate of soda gives a beautiful yellow precipitate of protophosphate of mercury.

Basic Oxalate of Mercury and Ammonia.—When freshly prepared protoxalate of mercury is mixed with dilute ammonia, a grayish-black powder is obtained, the composition of which is stated by Harff to be $=3Hg^2O, NH^3, C^2O^3$. The authors found the composition of this body to be very variable.

Oxalate of Silver, $\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O^2+C^4O^6$, loses nothing in weight at 212° F. At 230° F. it begins to decompose. At 302° F. silver remains. When suddenly heated to a higher temperatures it detonates. Wenzel's statement, that this salt forms a double salt with binoxalate of potash, was not confirmed by the authors. The salt is insoluble in oxalate of ammonia or soda.

Oxalate of Silver and Ammonia, $\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O^2, C^4O^6+4NH^3$, is obtained when anhydrous ammoniacal gas is passed over the dry salt. The salt swells up like a sponge, and acquires a considerable elevation of temperature. This compound dissolves in water; acids separate oxalate of silver from it.

If oxalate of silver be added to a solution of cyanide of mercury in hot water, and ammonia be then added, protoxalate of mercury separates, and the filtered solution contains

Cyanide of Silver and Ammonia, $2AgCy+NH^3$, which separates in brilliant, white, pearly, laminar crystals.

Oxalate of Cadmium, $2CdO, C^4O^6+6HO$.—When carbonate of cadmium is treated with oxalic acid, assisted by heat, it becomes

converted into oxalate of cadmium. It forms an amorphous powder, free from water. On the other hand, the addition of an excess of oxalic acid or oxalate of ammonia to a solution of chloride of cadmium produces a precipitate of crystallized oxalate of cadmium. One part of oxalate of cadmium requires 13,000 parts of cold and 11,000 parts of boiling water for its solution. Oxalic acid and acetic acid increase its solubility considerably. In alcohol it is absolutely insoluble. The mineral acids dissolve it with ease.

If oxalate of cadmium be heated to 644° F. in a bulb-tube, in a current of carbonic acid, there remains a mixture of metallic cadmium and oxide of cadmium.

Oxalate of Cadmium and Potash, $\left.\begin{matrix}\mathrm{Cd}\\ \mathrm{K}\end{matrix}\right\} \mathrm{O}^2, \mathrm{C}^4\,\mathrm{O}^6 + 2\mathrm{HO}$.—Oxalate of cadmium is added to a boiling solution of normal oxalate of potash, until a small excess remains undissolved; the solution is then filtered rapidly. On cooling, a heavy crystalline precipitate of oxalate of potash and oxalate of cadmium is formed. It consists of beautiful, clear, microscopic quadratic octahedra, containing 31·29 oxide of cadmium and 22·91 potash (calculated 31·72 CdO and 23·45 KO).

Oxalate of Cadmium and Ammonia, $\left.\begin{matrix}\mathrm{Cd}\\ \mathrm{Cd}\end{matrix}\right\} \mathrm{O}^2, \mathrm{C}^4\,\mathrm{O}^6 + 2\mathrm{NH}^3 + 4\mathrm{HO}$.—Oxalate of cadmium dissolves readily in oxalate of ammonia. According as the ammonia is more or less saturated with oxalate of cadmium, the salts obtained contain a larger or smaller amount of cadmium. The authors have prepared the salts—

$$2\left(\begin{matrix}\mathrm{NH}^3\\ \mathrm{Cd}\end{matrix}\right\} \mathrm{O} + \mathrm{C}^4\,\mathrm{O}^6 + 4\mathrm{HO}.$$

$$2\left(\begin{matrix}\mathrm{CdO}\\ \mathrm{NH}^4\,\mathrm{O}\end{matrix}\right\} \mathrm{C}^4\,\mathrm{O}^6 + 5\left(\begin{matrix}\mathrm{NH}^4\,\mathrm{O}\\ \mathrm{NH}^4\,\mathrm{O}\end{matrix}\right\} \mathrm{C}^4\,\mathrm{O}^6 + 18\mathrm{HO}.$$

$$2\left(\begin{matrix}\mathrm{CdO}\\ \mathrm{NH}^4\,\mathrm{O}\end{matrix}\right\} \mathrm{C}^4\,\mathrm{O}^6 + 6\left(\begin{matrix}\mathrm{NH}^4\,\mathrm{O}\\ \mathrm{NH}^4\,\mathrm{O}\end{matrix}\right\} \mathrm{C}^4\,\mathrm{O}^6 + 22\mathrm{HO}.$$

These double salts are decomposed when treated with water. Oxalate of cadmium separates.

Oxalate of Cadmium and Soda, $\left.\begin{matrix}\mathrm{Cd}\\ \mathrm{Na}\end{matrix}\right\} \mathrm{O}^2, \mathrm{C}^4\,\mathrm{O}^6 + 2\mathrm{HO}$, is obtained in the same way as the potash salt. It gave 33·95 CdO and 17·3 NaO (calculated 34·6 CdO and 16·8 NaO). It forms a crystalline precipitate, difficult of solution, consisting of microscopic quadratic octahedra.—Liebig's *Annalen*, ciii. p. 308.

On some Decompositions of Cinchonine. By Prof. von Babo.

The author submitted some of the cinchonine salts to the action of the galvanic current. After a preliminary experiment with the sulphate, which was found to be unacted upon by the current from a Bunsen's battery of eight cells, the nitrate was tried.

A solution of nitrate of cinchonine to which a few drops of nitric

acid was added to make it conduct, was exposed to the action of a Bunsen's battery of six cells, in an apparatus essentially like that used by Kolbe in his electrolytic experiments. After a short time the solution became brown, and gas was generated in some quantity: this was investigated at various periods of the reaction, but was found to have no constant composition. The chief constituent of that separated at the positive pole was oxygen, which after an hour was mixed with much carbonic acid. The latter disappeared, but after some time increased again in quantity. Besides a small quantity of hyponitric acid and binoxide of nitrogen, no other gas was observed. The gas collected at the negative pole was hydrogen, with some ammonia, and varying quantities of nitrogen. The action of the current was continued 24 hours, the apparatus being maintained at above 50° C., and nitric acid added to the electrolyte from time to time.

The liquid in which the positive pole dipped was of a clear wine-yellow colour. On examination it was found to contain nitrate of cinchonine. The liquid in which the negative pole was immersed had become considerably charged. It was of a deep red colour, and there was formed a large quantity of a resinous matter, which was readily soluble in alcohol and nitric acid. The author has not completed the investigation of this resinous alkaloid, which forms by far the greatest part of the products of decomposition.

The liquid in which the resinous mass was formed, was found to contain chinoline and formic acid. The author considers it probable that cinchonine is a copulated compound of chinoline with a methyle or formyle compound.

The hydrochlorate of cinchonine was similarly investigated. Chlorine, hydrogen, and oxygen were liberated in the gaseous form, and the liquid contained a body which was a mixture of chlorocinchonine and bichlorocinchonine. This had probably been formed by a secondary action of the chlorine (arising from the decomposition of hydrochloric acid) on the cinchonine.

From the results of his electrolytic experiments, the author was led to try the action of some methyle compounds on chinoline, particularly the action of sulphate of methyle on chinoline.

On bringing together these two substances, considerable elevation of temperature was experienced, but the subsequent application of heat was necessary to complete the action. The product was a liquid soluble in water, from which crystals were deposited. These are probably a salt of a copulated sulphamidic acid. The liquid on being treated with caustic potash or baryta became cloudy from the separation of oil drops, which at first red, became quickly green, and then violet, and on being gently heated changed into a beautiful violet mass. At the same time a gaseous body was liberated which excited violent sneezing and flow of tears.

To purify the violet substance it was separated from the alkaline solution, dissolved in water, so much sulphuric acid added that its colour disappeared, and then evaporated almost to dryness. The sulphuric acid was removed by baryta, on which the colour again

appeared, alcohol added, the sulphate of baryta filtered off, the excess of baryta removed from the filtrate by carbonic acid, the liquid again filtered and evaporated to dryness. The residue is a violet body which burns in the air with the formation of vapours smelling like aniline. It dissolves in water with a dark red colour, which verges to blue: soluble in alcohol with splendid violet colour. The aqueous solution evaporated to dryness yields a violet amorphous mass of brilliant cuprous lustre, which on standing in the air assumes a beautiful green colour. The colour is so intense that a drop of an alcoholic solution imparts a perceptible violet colour to a kilogramme of water. The substance is a feeble alkaloid. It dissolves in acids with change of colour; strong solutions becoming brown, and dilute ones colourless. The colour is instantaneously restored by alkalies, and even by carbonates of baryta and lime. This property of losing its colour by excess of acid, and its restoration by alkaline carbonates, would render it valuable in alkalimetric and acidimetric analyses, if it could be produced cheap. The appearance and disappearance of colour is sharper than with litmus, or with Schwarz's gallate of peroxide of iron.

On account of its play of colours the substance has been named *crisine*, and as sulphate of æthyle yields an analogous compound, they are distinguished as *methylic* and *æthylic crisine*. The formula has not been fixed, the analyses of different preparations gave different results; but some analyses agree closely with the formula $C^{22} H^{14} N^2 O^4$. Methylic crisine is not the only substance formed by the action of chinoline on sulphate of methyle, but as the other substances could not be purified, a further study was dispensed with.

Æthylic crisine was prepared and purified by an analogous method. Dry æthylic crisine is blue with a cuprous lustre, which exceeds that of sublimed indigo-blue. It is soluble in alcohol with deep violet or blue colour, which becomes redder when water is added to the solution. It has similar reactions to *methylic crisine*. The analyses seemed to point to $C^{26} H^{18} N^2 O^4$.

The reaction of sulphate of methyle and chinoline may be used as a ready means of detecting the smallest quantity of the latter body.—*Journ. für Prakt. Chemie*, lxxii. p. 73.

On some Compounds of Hippuric Acid.

By E. JACQUEMIN *and* SCHLAGDENHAUFFEN.

Hippuric acid is capable of combining with methylic alcohol to form hippurate of methyle. This æther, under the influence of ammonia, becomes converted into an amide. These are the new bodies that the authors have obtained and investigated.

I. *Hippurate of Methyle.*—Crystallized hippuric acid is dissolved in wood-spirit, and a current of muriatic acid is passed through the fluid, which is kept at a temperature of about 122° F., so as to boil it readily at the close of the operation. The syrupous liquid produced is treated with carbonate of soda to free it from the excess of muriatic acid; it is then taken up by æther, which, when spontaneously evaporated, leaves the hippurate of methyle in a crystal-

line form. To purify the crystals, they are recrystallized from boiling alcohol. When dried the analysis of these crystals gave—

	I.	II.	Average.
C	61·686	61·701	61·6935
H	5·654	5·692	5·6730
N	7·014	7·039	7·0265
O	25·646	25·568	25·6070

These numbers lead to the formula

$$C^{20}H^{11}NO^6 = C^{18}H^8NO^5, C^2H^3O.$$

It forms white, transparent, needle-like crystals. Under the microscope they are seen to be quadrangular prisms.

Hippurate of methyle is soluble in 120 parts of water at the ordinary temperature, and in 60 parts at 86° F. In boiling water it fuses at first, and forms a heavy oil which does not dissolve for some time. The supersaturated aqueous solution deposits crystalline needles.

It dissolves in alcohol, æther, and wood-spirit in all proportions. Water precipitates it from its solutions. It fuses at about 140° F., and on cooling affects a radiate structure. When the temperature is raised to between 248° and 284° F., it emits vapours which tarnish the apparatus; at 284° F. it becomes slightly yellow, and at 392° F. acquires the colour of the salts of platinum. Towards 482° F. the decomposition proceeds further; ammonia is evolved in abundance, benzonitrile distils off, and there remains a considerable quantity of carbon in the retort.

Fuming nitric acid causes the evolution of a gas which burns with a livid flame; when the air has not been completely expelled from the test-tube, the gas detonates on ignition, which is no doubt due to the production of nitrate of methylene. There remains a yellow body, which is probably nitrohippuric acid.

Alkalies dissolve methylhippuric æther, and decompose it when heated. Heated with potash in a retort furnished with a receiver, the distillate was combustible, and possessed the characteristic odour of wood-spirit. The regenerated hippuric acid was precipitated in combination with potash by muriatic acid.

II. *Hippuramide.*—A current of ammonia was passed into an alcoholic solution of methylhippuric æther, and left for three weeks in a closed flask. The solution was then set to evaporate spontaneously; in an hour an abundant precipitate formed, which evidently indicated the production of a new body, as the æther would have remained perfectly soluble under the same conditions. The body obtained being very slightly soluble in ordinary æther, this was used for its purification, by washing away the remaining hippurate of methyle. Analysis gave—

	I.	II.	Average.
C	58·076	58·105	58·0905
H	5·921	5·964	5·9425
N	15·375	15·384	15·3795
O	20·628	20·547	20·5875

These numbers correspond with the formula

$$C^{18}\,H^{10}\,N^{2}\,O^{4} = NH^{2},\ C^{18}\,H^{8}\,NO^{4}.$$

Hippuramide dissolves at the ordinary temperature in 100 parts of distilled water, in 80 parts of wood-spirit, and in 60 parts of alcohol. It is not acted upon by potash in the cold, but when boiled evolves ammonia violently. The potassic solution, afterwards treated with an acid, gives a precipitate of hippuric acid.—(*Comptes Rendus*, December 14, 1857, p. 1011.

On Combinations of Mannite with Lime, Baryta, and Strontia

By Joseph Ubaldini.

When an earthy oxide is brought into contact with a concentrated solution of mannite, and the mixture is agitated for a few minutes, a more or less alkaline liquid is obtained. This fact is explained by the affinity of mannite for the bases, analogous to that presented by the same bodies towards sugar, glycerine, and other substances of the same order.

I. *Compound of Mannite with Lime.*—If a mixture of 200 grms. of mannite, 66 grms. of slaked lime, and 660 grms. of water be left to itself in a well-stopped bottle, and shaken from time to time for two days, the solution will contain mannite and lime nearly in the proportions of their equivalents. This is what the author calls the *normal solution*. On pouring in three or four times its volume of alcohol, there is an immediate deposition of white flakes of a compound of mannite and lime, which collect at the bottom of the vessel, and adhere strongly. The liquid is decanted, and the deposit dissolved in its volume of water; it is again precipitated by alcohol, and these operations are repeated a third time, the last precipitate being carefully washed with dilute alcohol upon a filter. It must always be protected from the carbonic acid of the air. In this way a perfectly definite compound of mannite and lime is obtained in a pure state. From its analysis this compound may be represented by the formula $C^{6}\,H^{7}\,O^{6},\,CaO$.

The limpid solution of this compound, like that of saccharate of lime, sets into a mass on the application of heat. The coagulation commences at 185° F., and becomes complete at 194° F. As the temperature becomes lower, it regains its fluidity by degrees and attains its original limpidity at 122° F. If the solution be ever so little diluted with water, the coagulation does not take place.

Besides this monomannitate of lime the author has obtained another compound by the spontaneous evaporation of a solution, prepared in the same way, *in vacuo* over sulphuric acid. After the lapse of some days, fine crystals of mannite containing 3·5 per cent. of lime were formed. The supernatant fluid being decanted and left to itself for a few weeks, a white mass of crystalline appearance was deposited at the bottom of the capsule, and the mother-liquor was found to be very rich in lime. From its analysis the substance thus formed is a bimannitate of lime,—

$$CaO,\,2C^{6}\,H^{8}\,O^{6}.$$

Lastly, when the normal solution is heated to 212° F., a deposit is formed containing about one-half of its weight of lime; this is probably a basic compound,—

$$C^6 H^7 O^6, 3CaO.$$

II. *Compound of Mannite with Baryta.*—A compound of mannite with baryta is obtained in the same way as the mannitate of lime, by substituting for this base an equivalent quantity of baryta. On the addition of alcohol there is the same production of white flakes, which line the walls of the vessel, and at last collect at the bottom, forming a sort of very dense syrup. By solution in water and precipitation by alcohol, this syrupous compound is purified. Its formula is

$$2BaO, C^6 H^7 O^6.$$

III. *Compound of Mannite with Strontia.*—The preparation of this compound is exactly the same as that of the preceding, but it is remarkable that these two compounds, although nearly identical in physical properties, possess a different chemical composition. The results of the author's analyses of the strontia salt, although somewhat variable, lead to the formula,—

$$SrO, 2C^6 H^7 O^6.$$

Thus the compounds obtained are—

Mannitate of lime	$CaO, C^6 H^7 O^6$.
Bimannitate of lime	$CaO, 2C^6 H^7 O^6$.
Basic mannitate of baryta	$2BaO, C^6 H^7 O^6$.
Bimannitate of strontia ..	$SrO, 2C^6 H^7 O^6$.

Comptes Rendus, Dec. 14, 1857, p. 1016.

ANALYTICAL CHEMISTRY.

On some Reactions of Morphia. By Ludwig Kieffer.

Morphia precipitates hydrated peroxide of copper from the solution of peroxide of copper in ammonia. This is the case also with acetate of morphia; a neutral morphia salt is decomposed by an ammoniacal solution of copper completely saturated with hydrated peroxide of copper in such a way that 1 equiv. of ammonia passes to the acid of the morphia salt, and the morphia set free decomposes a second molecule of the oxide of copper and ammonia, fixes the ammonia and separates another equivalent of hydrated peroxide of copper. In such a decomposition, therefore, 2 equivs. of peroxide of copper represent 1 equiv. of morphia, when this is separated from a perfectly neutral salt.

In the same way oxide of silver is thrown down by morphia salts from a solution of oxide of silver in ammonia, and in the same quantitative proportions as were stated for oxide of copper. The oxide of silver is then reduced even in diffused daylight. The silver may be separated by filtration, and that in the filtrate determined by by Mohr's method. This determination, compared with the amount of silver employed, gives the quantity of silver separated by the

morphia; and supposing that each equivalent of morphia corresponded with 2 equivs. of silver, we should have an exact volumetrical method of analysis for morphia.

Morphia reduces ferridcyanide of potassium in solution to ferrocyanide. Although the process of decomposition could not be explained, the author found that 1 equiv. of morphia corresponds to 1 equiv. of ferridcyanide of potassium. This behaviour may also serve for the detection of morphia. If the solution of a morphia salt with alkali, in excess be mixed upon a watch-glass with a little ferridcyanide of potassium and immediately neutralized with muriatic acid, as the reduction takes place instantly, the addition of perchloride of iron produces prussian blue.

This behaviour was employed by the author in investigating the amount of morphia in opium by a volumetric method, for which he gives the following directions:—

1 grm. of powdered opium is mixed with 1 grm. of pure dry ferridcyanide of potassium, and reduced to the finest powder in a porcelain mortar; a very little water is added and thoroughly mixed with it. To this 1 grm. of solution of chloride of calcium is added, and the whole is then diluted to 150 cub. centims. The flask is shaken and left standing for some time. It is then filtered into another flask. A tolerably abundant precipitate has by this time been formed, containing, amongst other things, the meconic acid combined with lime. If chloride of calcium be again added to a portion of the filtrate, no further precipitate is produced. For the purpose of experiment, 15 cub. centims. of this filtrate are measured off, as the tenth part of 100 cub. centims. of fluid, and consequently the tenth part of a grm. of opium. This must contain exactly so much undecomposed ferridcyanide of potassium as is present beyond the coefficient of decomposition. A sufficient quantity (0·1 grm.) of iodide of potassium with starch-paste and an excess of muriatic acid is added, and a normal fluid of $\frac{2}{10}$ths of hyposulphite of soda is allowed to flow from a finely divided burette until the starch reaction is very weak; the number is then read off. The whole operation, however, must go forward as continuously as possible, because the iodine reaction soon occurs again in the strongly acid fluid, but this time due to a second separation of iodine.

Each cubic centimetre of the solution of hyposulphite of soda is $=\frac{1}{10000}$ atom of ferridcyanide of potassium, or 0·032933 grm. The number of cubic centimetres of hyposulphite of soda which was necessary to get rid of the iodine reaction, multiplied by this weight, gives the number of milligrms. of the undecomposed ferridcyanide, and the latter deducted from 100 milligrms., as the tenth part of the entire quantity of the salt, shows how much ferridcyanide of potassium has been decomposed by the morphia present; then as 1 equiv. of morphia reduces 1 equiv. of ferridcyanide of potassium, 0·032933 grm. of the latter is =0·0310 of crystallized morphia ($C^{35}H^{20}NO^6+2Aq$), or 0·0292 grm. of anhydrous morphia. The atomic weight of the anhydrous or hydrated morphia is therefore multiplied by the number of milligrammes of the decom-

posed ferridcyanide of potassium; the product is divided by the atomic weight of the ferridcyanide of potassium, and the quotient gives the amount of morphia in milligrammes, and consequently as a per-centage amount. As there is sufficient fluid, the analysis may be repeated eight or nine times. As the powdered opium of the apothecaries, when of fair quality, contains on an average 7 per cent. of crystallized morphia, the author indicates how important it is that all opium which is to be employed as medicine should be tested as to its amount of morphia. No opium should be sold that contains less than 6 per cent.—Liebig's *Annalen*, ciii. p. 271.

PROCEEDINGS OF SOCIETIES.

Royal Society.

November 26, 1857. (Major-Gen. Sabine, R.A., Treasurer and V.P., in the Chair.)

"Researches on the Cinchona Alkaloids." By W. Bird Herapath, M.D. Lond., F.R.S.E.—Part I.

In consequence of the gradually increasing scarcity of the *cortex cinchonæ calysayæ* and its chief product quinine, many other barks have been introduced into commerce, which furnish alkaloids having a strong general resemblance in the physical characters of those preparations of them more commonly employed in medicine, but differing widely in medicinal properties and commercial values.

In order to prevent fraudulent adulterations, it has long been highly desirable to have some ready methods of detecting admixtures of these alkaloids and their salts. The author having discovered several optical salts of these vegetable alkaloids, proposes to make their well-marked optical characters the means of such detection, and in the second part of this paper has fully developed his views upon this ready method of analysis, whilst in the present part he has passed under review the various existing tests for the different cinchona alkaloids, and the results of his investigations may be enumerated under the following conclusions:—

The following different methods of detecting the various cinchona alkaloids have been proposed:—

To Bouchardat and Pasteur we are indebted for the use of polarized light as a means of discriminating these alkaloids by the rotatory power which they exercise upon its plane.

Liebig employs the difference of their solubility in ether for the same purpose.

Almost all the other tests proposed have for their object only the discovery of quinine.

Professor Stokes employs fluorescence, combined with the peculiar reaction, in respect to this phenomenon, of hydrochloric acid, alkaline chlorides, &c. Brandes, the green reaction produced by the successive addition of chlorine and ammonia, whilst Vogel has modified this latter test in several ways.

Pelletier has employed the agency of a stream of chlorine gas, and Marchand uses nascent oxygen, obtained from puce-coloured oxide of lead and sulphuric acid for the discovery of quinine.

Leers first proposed a combination of Liebig's ether test, with that of Brandes's chlorine and ammonia reaction, as a means of establishing the purity of cinchonidine (miscalled by him quinidine, in common with all German chemists).

De Vry has advised the employment of hydriodic acid or iodide of potassium in order to discover the quinidine of Pasteur.

Van Heijningen depends on oxalate of ammonia to discriminate quinine from quinidine.

All these different tests the author has examined most critically, and, as far as it is possible to do so, determined the absolute numerical value of each method experimentally with the following results:—

He first explains MM. Bouchardat and Pasteur's researches on these remarkable alkaloids, from which it appeared that quinine and cinchonidine are powerfully lævogyrate, quinidine and cinchonine pre-eminently dextrogyrate, and that quinicine and cinchonicine are only slightly dextrogyrate upon plane-polarized light. These eminent experimenters determined also with accuracy the amount of these molecular rotations for each alkaloid. Yet the expensive nature of the apparatus, the complex formula requisite to reduce the observed amount of angular rotation to the normal molecular standard, and the many interfering actions necessary to be guarded against, effectually prevented this from ever becoming a process for general adoption, either among chemists or manufacturers.

Another method of recognizing the presence of quinine is founded on the optical phenomena of fluorescence, which have been investigated by Professor Stokes. Whilst endeavouring to turn this process to account in the quantitative estimation of quinine by means of excessive dilution, and marking the points at which the various phenomena of "epipolism," "fluorescence," and "internal dispersion" vanish, the author arrived at the following extraordinary results; premising that he employs the term "internal dispersion" to mean the positive, "fluorescence" the comparative, and "epipolism" the superlative degrees of the same optical power:—

I. Solutions containing 1 grain in 35,000 of either quinine or quinidine of Pasteur, exhibit epipolism and fluorescence; solutions with 1 grain in somewhat less than 140,000 grains of water are still fluorescent, with slight internal dispersion.

When diluted with from 3 to 10 gallons of water, these alkaloids continue to exhibit internal dispersion.

Solutions of quinicine are only slightly epipolic, and if the change has been perfect, scarcely at all fluorescent, but nevertheless strongly absorptive of rays of high refrangibility.

Cinchonidine also exhibits optical phenomena, but in a much slighter degree; about $\frac{1}{100}$th part of that of either quinine or quinidine.

Cinchonine is also fluorescent about $\frac{1}{120}$th part of the same alkaloids.

II. That on mixing fluorescent solutions of quinine, quinidine, or other cinchona alkaloid with the soluble chlorides, although all traces of optical phenomena are lost to the eye, yet the media still possess powerfully absorbent powers on the rays of high refrangibility, and, if sufficiently concentrated, are wholly opaque to them, without exhibiting any of the phenomena of dispersion, and greatly impede chemical action.

This was proved by three methods of observation:—

1st. By introducing vessels containing fluorescent solutions of quinine into other vessels filled with non-fluorescent solutions of the alkaloids, produced by previous admixture with chloride of ammonium, when all optical phenomena disappeared from the inner vessel.

2ndly. By surrounding fluorescent specimens of fluor-spar with these prepared solutions of the alkaloids, when the blue colour in the spar immediately disappeared.

3rdly. By photography; employing concentrated solutions of quinine mixed with chloride of ammonium in troughs to intercept the incident light from any object anterior to the camera, when it was found almost impossible to obtain any image upon the sensitive collodion plate, although the intensity of the visible image received on the ground-glass screen did not suffer any apparent diminution.

4thly. By photographic printing; troughs containing these solutions obstructed the chemical rays very considerably, thus interfering with the production of a positive picture from the negative, much longer exposure being necessary to produce any chemical effect.

III. That certain reagents do not destroy fluorescence; others only mask its appearance by their own colour; whilst some destroy it by neutralizing the excess of acid; others do so by producing salts which are themselves non-fluorescent media. Whilst a third class destroy it by really modifying the alkaloid itself.

IV. That as so many reagents of common occurrence interfere with the manifestation of fluorescence, and as it is also a property common to all the cinchona alkaloids herein described, its appearance becomes no longer of any value as a test for quinine.

V. Brandes's chlorine and ammonia test will discover 1 grain of either quinine or quinidine in 1 gallon of water, but shows no difference between these alkaloids, except in very concentrated solutions, when there is a precipitate with quinidine, but not with quinine.

Quinicine is also influenced by this test, but less extensively.

VI. Dr. Vogel's first modification of this test is of no apparent value; but by also employing ammonia, the author has found that it will indicate both quinine and quinidine, detecting readily 1 grain of either in a pint, and showing slight evidence with 1 grain in 10,000 grains of water.

There is scarcely any reaction with quinicine.

VII. Dr. Vogel's other modifications of Brandes's test are unimportant, with the exception of the fourth, viz. excess of chlorine, and very little ammonia. This detects 1 grain in about 2000 grs. of

fluid very readily, if excess of acid be avoided at first. The test, however, is equally indicative of quinidine; it gives scarcely any perceptible reaction with quinicine.

VIII. Pelletier's chlorine gas-test succeeds very well with the free alkaloids, but does not show any indication with their salts. It is equally capable of detecting quinidine, and gives the same phenomena.

IX. Marchand's test is not a delicate reaction.

X. All the foregoing tests, although specially proposed for the discovery of quinine, possess equal powers and show the same appearances with quinidine. But they have no reaction on cinchonine, cinchonidine, or cinchonicine.

XI. Van Heijningen's test by oxalate of ammonia, produces, after some hours, a crystalline oxalate of quinine, when using a fluid containing only 1 grain of alkaloid in 800 grs. of water, and very readily detects immediately 1 part in 350. It does not precipitate quinidine or cinchonidine, but it produces a white precipitate in concentrated solutions of cinchonine.

XII. De Vry's test for quinidine by hydriodic acid, or iodide of potassium in neutral solutions, produces a well-marked crystalline precipitate as a colourless salt, when one part of the alkaloid is present in 1000 of the fluid; the crystals, being short hemihedral prisms, are readily recognized; the neutral hydriodates of cinchonidine are colourless, silky, prismatic needles, and much more soluble. If to a solution of the sulphate of quinidine in dilute spirit ($\frac{1}{5}$) we add hydriodic acid, and expose to the action of light during some days, there is formed the red iodo-sulphate of the author.

The neutral hydriodate of quinine appears as lemon-yellow prisms. The neutral hydriodate of cinchonine appears as long, thick, colourless prisms, and is very soluble.

XIII. Liebig's ether test dissolves quinine, quinicine, and cinchonicine, and therefore does not discriminate between them, as they are all uncrystallizable. It dissolves also a portion of the quinidine and cinchonidine. Should the proportions of these alkaloids not exceed the solvent powers of the ether employed, they will not be indicated by this test. When crystallization occurs, the rhombic prisms indicate cinchonidine; the long slender aciculæ, quinidine; whilst an amorphous powder is demonstrative of cinchonine. Ether also extracts cinchonidine from cinchonine; but its sparing solubility in ether necessitates the employment of warmth, and a large quantity of ether.

XIV. Leers' combination of the ether test with that of Brandes can readily detect small portions of quinine, quinidine, or quinicine in cinchonine or cinchonidine, especially when used in the manner as modified by the author.

Dec. 10. (The Lord Wrottesley, President, in the Chair.)

"On the Molecular Properties of Antimony." By George Gore, Esq.

Antimony may be readily deposited by the electro-process from either of the following liquids:—5 parts of tartar-emetic and 5 parts

of tartaric acid dissolved in a mixture of 2 parts of hydrochloric acid and 30 parts of water; or 3 or 4 parts of tartar-emetic dissolved in 1 part of the ordinary chloride of antimony.

The metallic deposits obtained from these two liquids differ greatly in appearance, in structure, and in physical properties: that obtained from the first liquid has a silver-grey colour and frosted surface, is hard in texture, and has a beautiful radiating crystalline structure; whilst that obtained from the second liquid has the colour and appearance of highly polished steel, and has a bright metallic amorphous fracture. The specific gravity of the former is 6·55, whilst that of the latter is 5·78, both being somewhat variable in this respect. The electro-chemical equivalent of the crystalline variety, after deducting a small portion of gas contained in it, is about 40·2; and of the amorphous kind, after deducting a much larger per-centage of gas and of chloride of antimony, which it always contains, the same; but the equivalents actually obtained, including those substances, were 40·7 for the crystalline and 43·3 for the amorphous variety. Amorphous antimony was found to be electro-positive to the crystalline kind, both in acids and alkalies; it was also thermo-electro-positive to that substance; and both reduced silver by immersion in a solution of nitrate of silver.

Both these substances when deposited are in unequal states of cohesive tension at their two surfaces, frequently in so great a degree as to rent the metal in all directions. But the most remarkable circumstance, and of which a brief account was published in the Philosophical Magazine, January 1855, is, that amorphous antimony is liable, by percussion or heat, to undergo a rapid and intense molecular change throughout its mass, consisting apparently of a violent commotion amongst its particles, similar, but in a much higher degree, to the changes already observed by other experimentalists in sulphur, selenium, iodide of mercury, &c., and attended by evolution of an extraordinary amount of heat, sufficient, when the substance is massive, to raise its temperature from 60° to upwards of 450° Fahr., melting in several instances bars of tin and other metals.

During the action the chloride of antimony and a portion of the gas are expelled by the heat, and the substance loses its remarkable property. After the action the antimony is found to have undergone no oxidation, but to have considerably altered in its physical characters; it has lost its steel-bright colour and become comparatively grey, and has acquired a dull grey granular fracture; its specific gravity has also increased, and it has evidently passed a considerable stage towards the condition of the other variety. The grey metal undergoes no such change.

By careful trituration of thin pieces of the amorphous metal under cold water, it has been obtained in the state of a fine powder possessing the same molecular property. The chloride of antimony adheres to the metal with considerable force, and is only partly removed by digesting the powder in dilute hydrochloric acid for a week; and the gas contained in both varieties is only expelled by pressing them.

THE CHEMICAL GAZETTE.

No. CCCLXVIII.—February 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Alcoholic Fermentation. By L. PASTEUR.

THERE are two principal cases to be distinguished in alcoholic fermentation. Yeast acts in sugar and water when pure, or in presence of albuminoid matters. In the former case the yeast becomes exhausted and unfit for exciting fermentation again. In the second case it remains active, and more is collected than was employed. It is destroyed as much as in the first case, but as a fresh portion is formed, the weight of that which has disappeared is masked by the increase of weight due to that which is regenerated. The weight of the yeast that disappears is calculated by authors at about $1\frac{1}{2}$ part of dry yeast to 100 parts of sugar.

The decomposition of yeast when the ferment is exhausted in contact with pure solution of sugar, is one of the facts which is of the most consequence to Liebig's theory. He says, "If fermentation were a consequence of the development and multiplication of the globules, they would not excite fermentation in pure sugar-water, destitute of the other conditions essential to the manifestation of vital activity; this water does not contain the nitrogenous matter necessary for the production of the nitrogenous part of the globules."

There can be no doubt that if well washed yeast in contact with pure sugar-water only alters and destroys itself, it is impossible to assert that alcoholic fermentation is a correlative action of a development of the globules. Experiment shows that the facts upon which Liebig depends are not so exact as he supposes, and that in fermentation with pure sugar-water, there is a sum of life and organization equal to that manifested in the general case.

Of two equal quantities of fresh yeast, washed with much water, one was placed in fermentation with pure sugar-water, and after all the soluble part of the second had been extracted by boiling with water and filtering it to remove the globules, as much sugar was added to the limpid liquid as was employed in the first fermentation besides a trace of fresh yeast, the weight of which could not disturb the results of the experiment. The globules soon bud out, the liquid becomes turbid, a deposit of yeast is formed by degrees, and at the same time the splitting-up of the sugar takes place and is perceptible in the course of a few hours. By thus causing the organization into globules of the soluble part of the second portion of yeast, a consi-

derable quantity of sugar is decomposed. In one experiment 5 grms. of yeast fermented 12·9 grms. of sugar in six days, when they were exhausted. The soluble portion of 5 grms. of the same yeast fermented 10·0 grms. of sugar in nine days, and the yeast developed was also exhausted.

Thus when we excite the organization into globules of the soluble nitrogenous portion of yeast, it decomposes a quantity of sugar approaching the total weight that may be split-up by a portion of crude yeast equal to that from which the soluble matter was extracted. The difference between the two weights appears easy to be understood. The development of the globules must be difficult in very dilute yeast-water, and boiling water does not easily remove all the soluble part, which is probably imprisoned in the interior of the globules.

M. Thenard long since observed that yeast might be dried at 212° F., or boiled, without sensibly losing its energy. The peculiarity of its action under these special conditions, consists in the fermentation taking place more slowly than with the same yeast in a fresh state, and being of longer duration. These curious facts are also cited by the chemists who share the opinions of Liebig and Berzelius, and deny the influence of organization in the causation of the phænomena; for a temperature of 212° F. should destroy all life in yeast, and yet it acts after exposure to this temperature, with or without a prolonged desiccation.

The author has shown that in yeast it is not the globules that play the principal part, but the formation of globules from their soluble part, for the formed globules may be suppressed, and the total effect is perceptibly the same. Now it is certainly of little consequence whether they are suppressed by filtration, with separation of their soluble portion, or killed by a temperature of 212° F. The latter is the case when yeast dried at 212° F. is employed, and also with yeast boiled with water, when the dissolved part is not separated by filtration. If the boiled yeast is filtered, the globules collected on the filter will be almost inert.

But how can the fermentation of sugar be effected by the employment of yeast exposed to a temperature of 212° F., if it be due only to the organization of the soluble part of the globules, when these have been paralysed by the temperature of 212° F.? Fermentation is then set up just as in a natural saccharine liquid, the juice of the grape, sugar-cane, &c., that is to say spontaneously, and this explains the peculiarity indicated of the retardation of the fermentation when the yeast is dried at 212° F., just as that explains the longer duration of its action under those conditions. In all cases, even those which are apparently most apt to prevent us from believing in the influence of organization in the phænomena of fermentation, we see that the chemical action by which they are characterized, is always correlative with a slow and progressive formation of globules like the chemical action itself.

The following observations, in confirming the preceding data, throw a new light upon fermentation. The theories of fermentation

start from the principle that the ferment neither yields nor takes anything from the fermentescible matter. The author shows, on the contrary, that the yeast draws something from the sugar, that the sugar is one of its aliments, and there is no equation between the quantities of alcohol, carbonic acid (lactic acid), and the total quantity of sugar which has become uncrystallizable. Two equal quantities of fresh-washed yeast are taken, one of them is dried in the capsule in which it was weighed, and its exact weight at 212° F. is taken. This weight will always be less than that of the other portion dried at 212° F., but collected after it has been exhausted in presence of an excess of sugar. The difference of weight is variable, but always distinct, and it must be observed that there are important causes of loss for the portion of yeast which weighs the most. This curious and unexpected result accounts for a fact which greatly astonished the author at the commencement of his investigations. When yeast exhausts itself in pure sugar-water, it is assumed that all its nitrogen passes to the state of ammoniacal salt. The quantity of ammonia formed during fermentation is really excessively small, and much less than that which should be produced in order to account for the loss of nitrogen in the yeast. This loss is only apparent. It is due principally to the increase of weight of the yeast by the assimilation of sugar.

The conclusions to be deduced from the preceding facts must be evident to everybody. The splitting-up of sugar into alcohol and carbonic acid is an action correlative with a vital phænomenon, an organization of globules, in which sugar takes an immediate part, by furnishing a portion of the elements of the substance of these globules.

The author has also discovered a mode of fermentation of tartaric acid, which applies very readily to ordinary dextro-tartaric acid, but scarcely, if at all, to lævo-tartaric acid. Now when the paratartaric acid formed by the combination of the two tartaric acids is submitted to the same mode of fermentation, it becomes split into dextro- and lævo-tartaric acids, of which the former ferments, whilst the latter remains intact, so that one of the best modes of isolating lævo-tartaric acid consists in splitting paratartaric acid by fermentation. The nature of the products of fermentation of tartaric acid, compared with that of new acids found by the author in the fermentation of ordinary sugar, and coupled with some curious crystalline forms of sugar-candy and detro-tartaric acid, lead to the opinion that sugar-candy probably has the same molecular constitution as that acid.—*Comptes Rendus*, December 21, 1857, p. 1032.

Researches upon Cochineal. By M. Schutzenberger.

Manufacturers of printed cottons have long known that cochineal when left for several days in contact with an aqueous solution of ammonia, undergoes an interesting modification which has not yet attracted the attention of chemists. The red colouring matter (carminic acid) passes to the state of a matter of a fine violet

colour, which acids do not modify, or cause to become red. This body cannot, therefore, be regarded as carminate of ammonia. To ascertain the transformation that takes place, I analysed some carminic acid, upon the purification of which I had bestowed the greatest care, and modified this acid by means of ammonia. By the comparison of the two results obtained, I found that the colouring matter of the ammoniacal cochineal was the amide of carminic acid. On analysing carminic acids prepared by different processes, I found that each had a different composition, but all my analyses might be definitively represented by the same formula with more or less oxygen, and I concluded therefrom that there exists at least two degrees of oxidation of carminic acid. I have in fact succeeded, by employing æther mixed with more or less alcohol as a solvent, in separating and obtaining in a crystalline form two products, of which one is represented by the formula

$$C^{18} H^{8} O^{10},$$

and the other by

$$C^{18} H^{8} O^{14},$$

as well as two intermediate degrees of oxidation, one

$$C^{18} H^{8} O^{12},$$

the other

$$C^{18} H^{8} O^{13},$$

which may be regarded either as peculiar bodies, or as compounds of the more oxidized with the less oxidized acid. By heating a mixture of carminate of soda and iodide of æthyle to 257° F. in a closed tube, I have obtained the æthers of these carminic acids in the form of red bodies, insoluble in water, but soluble in alcohol.

I have also remarked that nascent hydrogen completely decolorizes a solution of carminic acid, and that the colour returns in the air. This reaction may be compared with that which takes place when indigo is reduced.—*Comptes Rendus*, January 4, 1858, p. 47.

Note on the Constitution of the Acetones. *By* C. Friedel.

Chancel and Gerhardt were the first to regard the acetones as bodies homologous with the aldehydes, that is to say, as aldehydes in which one molecule of hydrogen is replaced by an alcoholic radical. Williamson's experiments support this view; that chemist, by distilling a mixture of acetate and valerianate of potash, obtained a mixed acetone intermediate between those corresponding with the acids employed. What Williamson has done for the series of fatty acids, may be extended to that of the aromatic acids.

By distilling a very intimate mixture of acetate and benzoate of lime, obtained by saturating with milk of lime a mixture of equivalent weights of crystallizable acetic acid and benzoic acid, and treating the product by fractional distillations, a limpid and almost colourless liquid is easily separated. It possesses an agreeable odour, very like that of oil of bitter almonds, boils at 388° F., and solidi-

fies at +57° F. in large crystalline laminæ. Its density at 59° F. is 1·032. Its composition is—

	Calculated.	Found.	
C	80·00	80·00	80·15
H	6·66	7·39	6·87

corresponding with the formula

$$C^{16} H^{8} O^{2}.$$

Its theoretical density of vapour for 4 volumes is 4·15; that given by experiment at 525°·2 F. is 4·27.

The liquid obtained is very near to hydruret of benzoyle, $C^{14} H^{6} O^{2}$, and may be derived therefrom by the substitution of a molecule of methyle for one of hydrogen:—

$C^{14} H^{5} O^{2}$	$C^{14} H^{5} O^{2}$
H	$C^{2} H^{3}$
Hydruret of benzoyle.	Methyluret of benzoyle.

It is therefore a true mixed radical, a methyluret of benzoyle, just as ordinary acetone is a methyluret of acetyle.

Ammonia and bisulphite of soda appear to act with difficulty upon methyluret of benzoyle. Its formation is accompanied by that of a certain quantity of acetone, benzine, and a yellow, viscous liquid, which distils above 572° F., and resembles benzophenone.

By the distillation of a mixture of acetate and butyrate of lime, the author easily obtained the methyluret of butyryle,—

$$C^{8} H^{7} O^{2}$$
$$C^{2} H^{3},$$

as proved by the following analysis:—

	Found.	Calculated.
C	69·4	69·7
H	11·9	11·6

Palmitic acid did not furnish such good results; the small quantity of material at the author's disposal prevented him from isolating amongst the products of distillation, anything more than palmitone and a solid hydrocarbon.

The action of perchloride of phosphorus upon acetone agrees exactly with the theory supported by the preceding facts. Perchloride of phosphorus alters the hydrurets of the acid radicals by replacing their two molecules of oxygen with two molecules of chlorine. Thus hydruret of benzoyle, $C^{14} H^{6} O^{2}$, furnishes chlorobenzole, $C^{14} H^{6} Cl^{2}$. If acetone be a hydruret in which one molecule of hydrogen is replaced by $C^{2} H^{3}$, it should furnish an analogous compound, a methyluret of chloracetole with perchloride of phosphorus. This is what takes place. When a little acetone is poured upon perchloride of phosphorus, a very brisk reaction takes place, which must be moderated at the commencement by cooling the apparatus, and assisted at the end by a gentle heat. Muriatic acid is evolved, and the liquid contains oxychloride of phosphorus and two bodies, which are separated by washing with water and distilla-

tion. One of these substances boils at 158° F., and its composition is

$$C^6 H^6 Cl^2, \text{ or } \begin{matrix} C^4 H^3 Cl^2 \\ C^2 H^3 \end{matrix}.$$

It is isomeric with chloride of propylene. By the action of perchloride of phosphorus upon aldehyde, Wurtz has also obtained the compound $C^4 H^4 Cl^2$ boiling at 136°·4 F. with which methyluret of chloracetole is homologous. The other liquid, which is probably a product of decomposition of the former, boils at about 86° F., and has the formula $C^6 H^5 Cl$. It appears to have the same relation to methyluret of chloracetole that chlorinated æthylene has with chloride of æthylene.—*Comptes Rendus*, Dec. 14, 1857, p. 1013.

On Ammonio-oxide of Copper, a Solvent for Vegetable Fibre. *By* Dr. Ed. Schweizer.

The author prepared basic hyposulphate of copper, $4CuO, S^2 O^5$, by carefully precipitating a solution of hyposulphate of copper with dilute ammonia. The precipitate was filtered, washed, and then treated with strong ammonia, in which it very readily dissolved up to a dark blue liquid, from which, on cooling, crystals of cuprohyposulphate of ammonia, $2NH^3 CuO, S^2 O^5$, were deposited. Hence by dissolving the basic salt in ammonia, there must have been formed some ammonio-oxide of copper which remained in solution.

This blue liquid has the very remarkable property of dissolving vegetable fibre at ordinary temperature.

When clean cotton is treated with this blue liquid, it soon assumes a gelatinous consistence, the filaments separate and disappear, and after some kneading with a glass rod, the whole is changed into a mucous liquid. No heat is given out in this operation. If sufficient liquid has not been employed, a portion of the fibre remains visible; but on adding an excess and agitating it disappears, an almost colourless solution is obtained, which after dilution with water may be filtered.

On supersaturating the solution with hydrochloric acid, a voluminous white precipitate is formed, which, collected on a filter, has the appearance of moist hydrated oxide of alumina. This appears to be nothing more than cellulose, which is disorganized, but not essentially altered in its chemical nature.

When the gelatinous precipitate, thoroughly washed from salts, is suspended in water, iodide of potassium added, and then a little chlorine-water, the liquid becomes brown, a proof that neither starch nor amylaceous substances are present. Dried on the water-bath, the precipitate diminishes in bulk, and leaves a horn-like, transparent, brittle mass, resembling dried starch-paste, but having no taste. Heated in the air, it burns away without residue.

Paper and *linen* are also dissolved, though somewhat more slowly than cotton; and the solvent power extends to some animal tissues. *Silk* dissolves even more easily than cotton, and acids precipitate from the clear solution a gelatinous body. *Wool* is only dissolved

by the aid of heat. *Hair* is gradually decomposed by the liquid, but without effecting solution. *Bladder* swells at first, and afterwards dissolves. Starch is not dissolved by the liquid.

The solution of *basic sulphate of copper* in ammonia has the same properties as the above solution, and may, of course, be more easily prepared.—*Journ. für Prakt. Chemie*, lxxii. p. 109.

On the Action exerted by the Mixture of an Oxidizing and a Reducing Body upon the Metals and their Oxides. By H. Debray.

Berthollet introduced the idea of mass into the explanation of certain apparently contradictory chemical phænomena. It is in this way that he explains how oxide of iron can be reduced by hydrogen, furnishing water, whilst metallic iron, under the same conditions of temperature, is converted into magnetic oxide with evolution of hydrogen. The author has endeavoured to verify this principle in some cases where its intervention appeared to be necessary, by the simultaneous action of a mixture of definite proportions of two bodies capable separately of producing opposite effects. Such mixtures are numerous, but there are two,—the mixture of carbonic acid and oxide of carbon, and that of aqueous vapour and hydrogen,—which merit a special examination on account of the great number of cases in which they are naturally produced, and then intervene in chemical reactions. It is important also, to fix the cases in which masses really intervene, and to distinguish them from those in which, as M. H. Sainte-Claire Deville has lately pointed out, there is a simple separation of the elements by a high temperature, giving rise to the phænomena of *dissociation*.

To produce mixtures in known proportions of aqueous vapour and hydrogen, the author passes hydrogen through a Liebig's tube containing water heated by the water-bath to a constant temperature throughout the experiment. The gas becomes saturated with moisture at the tension corresponding with the temperature of the water-bath, and then passes into a tube containing the matter to be experimented on. The condensation of the aqueous vapour is prevented by heating the parts of the apparatus traversed by the mixture, which afterwards escapes through an open tube. If the water-bath be at a temperature of 179°·6 F., the tension of the aqueous vapour is, according to M. Regnault, $=384^{m}\cdot435$, that is to say, about half an atmosphere. The tension of the hydrogen is therefore also half an atmosphere, so that the composition of the mixture may be represented by the formula H + HO.

If the temperature were 171°·6, it would be,

$$2H + HO.$$

The following are some of the results obtained with such mixtures:—If the mixtures

$$H + HO,\ 2H + HO,\ 3H + HO$$

be passed over sesquioxide of iron heated to redness, black protoxide of iron is always obtained. The magnet has no action upon

it; it is readily oxidized, and the product of its oxidation is the magnetic oxide. It may be dissolved without evolution of gas in muriatic acid, and dilute nitric acid attacks it with disengagement of nitrous fumes.

The mixture represented by the formula

$$4H+HO,$$

reduces sesquioxide of iron to the metallic state; and if the mixtures

$$3H+HO,\ 2H+HO,\ H+HO$$

be passed over this iron, the mixture is not acted on, so that there is a perfect equilibrium between the inverse action of water and hydrogen acting in these different proportions upon iron or its protoxide.

The mixture

$$CO^2+CO$$

also produces protoxide of iron by its action upon sesquioxide. It does not alter metallic iron, but reduces oxides of nickel, cobalt and zinc to the metallic state.

Molybdenum and tungsten do not decompose water even at a high temperature, so that it was probable that the hydrogen in the mixture would act upon their oxides as if no aqueous vapour were present. This, however, is not the case. Oxides of tungsten and molybdenum can decompose water at a red heat, and then become converted into tungstic and molybdic acids. By the action of mixtures upon tungstic and molybdic acids, the intermediate oxides may be easily obtained. In the mixtures

$$CO^2+CO,\ CO^2+2CO,$$

tungstic acid is converted into red oxide, TO^3, of fine colour.—*Comptes Rendus*, December 14, 1857, p. 1018.

Note on Valerianate of Atropine. *By* M. Miette.

The organic valerianates are at present very few in number. Beyond the valerianate of quinine, first indicated at the Scientific Congress of Florence in 1842, by Prince Louis Lucien Bonaparte, and investigated by him with great care, hardly any one was known except the valerianate of atropine.

To obtain this salt in the greatest possible state of purity, we must have recourse to the method employed by Prince Louis Lucien Bonaparte for the preparation of valerianate of quinine, as indeed was done by M. Michéa, who first procured it. A slight excess of valerianic acid is poured into a very concentrated alcoholic solution of atropine, and about twice its volume of distilled water is added to the mixture. Care must be taken to effect the saturation in the cold, as too intense a heat destroys the compound formed. The whole is exposed, in a shallow vessel, to spontaneous evaporation, or to the temperature of a warm chamber, not exceeding 122° F. The residue in the vessel after evaporation is valerianate of atropine.

Unlike valerianate of quinine, valerianate of atropine does not crystallize. It presents the appearance of a syrupous liquid, of a

bright yellow colour, which changes to orange in contact with the air. It has the fetid odour of valerianic acid, and deviates polarized light very slightly to the left. Its molecular rotatory power may be valued at −11·807. It is very soluble in water, and its solution, which is at first neutral, becomes acid by evaporation.

Infusion of gall-nuts produces in it a much less rapid and abundant precipitate than that which it causes in the solution of atropine. Chloride of gold produces in it a citron-yellow colour, without any very manifest precipitate. Tincture of iodine does not cause a brown colour.

The aqueous solution of valerianate of atropine produces no turbidity in chloride of barium, but it precipitates the neutral aqueous solution of nitrate of silver. The precipitate is soluble in much water, and disappears entirely on the addition of a few drops of nitric acid. If the aqueous solution of valerianate of atropine be treated with mineral acids, even with the weakest, valerianic acid, recognizable by its odour, is evolved.—*Comptes Rendus*, December 21, 1857, p. 1052.

Theory of Alcoholic Fermentation. *By* M. Maumené.

The new theory of alcoholic fermentation to which I have been led on the one hand by an attentive study of known facts, and on the other by the experiments which I have made on this subject, should not appear before my book upon Wines, &c.; but the Academy having lately received a communication by M. Berthelot, and more recently that of Mr. Pasteur, I do not think that I ought to wait longer before making known my own.

My theory leads to two remarks, to which I now call the attention of the Academy.

Remark I.—Sugar appears to be capable of conversion, by fermentation properly so called, into other alcohols besides ordinary alcohol. We have

1. $C^{12}H^{12}O^{12}=2C^4H^6O^2+4CO^2$,
2. 3 $=4C^6H^8O^2+12CO^2+4HO$,
3. $=C^8H^{10}O^2+4CO^2+2HO$,
4. 5 $=4C^{10}H^{12}O^2+20CO^2+12HO$,
5. 3 $=2C^{12}H^{14}O^2+12CO^2+8HO$.

Are these transformations, indicated by theory, realized in practice? Are they the result of simple fermentation? If my theory is well founded, it gives—

1. $\begin{cases} C^{12}H^{12}O^{12}-H^{12}+O^{12}= & 12CO^2, \\ C^{24}H^{24}O^{24}+H^{12}-O^{12}=6C^4H^6O^2; & \end{cases}$
2. $\begin{cases} C^{12}H^{12}O^{12}-H^8+O^{16}= & 12CO^2+4HO, \\ C^{24}H^{24}O^{24}+H^8-O^{16}=4C^6H^8O^2; & \end{cases}$
3. $\begin{cases} C^{12}H^{12}O^{12}-H^6+O^{18}= & 12CO^2+6HO, \\ C^{24}H^{24}O^{24}+H^6-O^{18}=3C^8H^{10}O^2; & \end{cases}$
4. .....
5. $\begin{cases} C^{12}H^{12}O^{12}-H^4+O^{20}= & 12CO^2+8HO, \\ C^{24}H^{24}O^{24}+H^4-O^{20}=2C^{12}H^{14}O^2. & \end{cases}$

Methylic alcohol does not appear in these formulæ, which cannot serve to explain its formation; this will not astonish anybody, as it is not observed in fermented liquids. But this is also the case with amylic alcohol, which leads us to regard this alcohol as derived from a different source from true fermentation. This is not impossible, for fermented liquids never have nearly their bouquet at the conclusion of the fermentation itself (with very few exceptions). Those odoriferous æthers, almost all amylic, are developed in course of time, under an influence different from that of the globules; consequently my theory cannot be shaken by this consequence, of which the future will show the correctness.

Remark II.—The tartaric acid of grapes appears to become converted into sugar by ripening. Its composition allows the conversion to be regarded as very simple; it is sufficient that the acid should lose oxygen and absorb hydrogen, to represent grape-sugar:—

$$3C^8\,H^6\,O^{12} + H^6 - O^{18} = 2C^{12}\,H^{12}\,O^{12}.$$

M. Pasteur has shown that racemic acid is always formed in the grape, and that this acid is formed of one-half of dextro- and one-half of lævo-tartaric acid. He has also demonstrated that bodies which act upon polarized light, often furnish, by their transformations, other bodies which act like them in the same direction. May we not assume from this, that grape-sugar is produced from racemic acid, the glucose being formed by the dextro-tartaric acid, and the chylariose by the lævo-tartaric acid? It is true that in this case grape-sugar should contain glucose and chylariose in equal proportions. But need this consequence completely destroy our hypothesis? May not the half of the glucose be destroyed by a foreign action? At least we must remain in doubt.—*Comptes Rendus*, December 14, 1857, p. 1021.

PROCEEDINGS OF SOCIETIES.

Royal Society.

November 26, 1857. (Major-Gen. Sabine, R.A., Treasurer and V.P., in the Chair.)

"Researches on the Cinchona Alkaloids." By W. Bird Herapath, M.D. Lond., F.R.S.E.—Part II.

In the former part of his paper, the author examined the existing tests for discriminating between the various cinchona alkaloids, and pointed out their insufficiency. In the present part, he shows that the optical characteristics of the iodo-sulphates of the alkaloids quinine and quinidine are sufficiently well marked to render the existence of *either one* of these alkaloids *certain*, and that although the iodo-sulphate of cinchonidine is very closely related optically and chemically to the homologous salt of quinine, yet there are sufficient points of dissimilarity to enable us to diagnose between the two; and, moreover, that the production of this salt is a beautiful means of deciding readily whether cinchonidine is present in specimens of

cinchonine or cinchonicine; all evidence of quinine or its allies having been decided in the negative by the results of the previous tests, as proposed by Brandes, Vogel, Pelletier, Leers, or the author.

The cinchonidine of Wittstein has also, by the same method, been proved by the author to be totally different from the cinchonidine of Pasteur.

Acetic acid and chloroform may also be employed for discriminating between cinchonine and cinchonidine.

The *chemical characters* of all these iodo-salts furnish no means of discrimination, for as a class they all agree in being more or less soluble in spirit, giving a deep sherry-brown solution, from which water precipitates them in an amorphous form, as dark brown, cinnamon-brown or purplish-brown coloured precipitates; they are only very slightly soluble in dilute spirit, and scarcely at all in water, ether, turpentine, or chloroform: acetic, dilute sulphuric, or hydrochloric acid have but little action upon them, whilst concentrated hydrochloric or sulphuric acid decomposes them. Nitric acid rapidly acts upon them, even in the cold, with violent evolution of nitrous acid and production of heat, iodine being oftentimes liberated in the crystalline form.

Alkalies also decompose them.

Sulphuretted hydrogen, soluble sulphides, sulphurous acid and sulphites, together with chlorine-water, instantly decolour their alcoholic solution, with the production of hydriodic acid.

In dilute alcoholic solutions, starch gives immediate evidence of iodine, and nitrate of silver gives a yellowish-white precipitate of iodide of silver, and some organic basic compound which can only be removed by the action of concentrated boiling nitric acid; this reaction, although commencing at the ordinary temperature, with violent disengagement of nitrous acid vapours, must be perfected by boiling.

Baryta salts exhibit the existence of sulphuric acid, which in all instances is an essential constituent in their formation.

The quinidine and cinchonine salts dissolve with more difficulty, in consequence of their greater thickness and less extent of surface.

Since the author had the honour of communicating his discovery of the optical salt of cinchonidine to the Royal Society (a preliminary notice of which was published in the Chem. Gaz. vol. xv. p. 96), he has ascertained that its primary form is, like that of the quinine salt, that of a right rhombic prism, and usually very thin, but having for its acute angles 43°, and 137° for its obtuse, with the rectangular axes $M^a_{2\cdot482}$; $T^a_{1\cdot000}$; P^a_{00001}—the quantity for P^a being variable and very minute. In a former communication to the Royal Society, the quinine salt was shown to have a primary rhombus, having 65° for the acute, and 115° for the obtuse angles, with the three rectangular axes, thus related:—$M^a_{1\cdot87}$; $T^a_{1\cdot000}$; P^a_{01000}.

In both salts the optical characters are usually examined through the shortest axis, P^a: in some recent observations on the quinine salt, the author has discovered that it transmits a *blood-red* beam of plane-polarized light through the axes M^a and T^a, and this is also a beam polarized in a plane parallel to that of the axes M^a and T^a.

TABULAR VIEW.

Both the quinine and cinchonidine salts are derivable from the primary rhombic prism, and crystallize as rhomboids and β-prisms . . . . . } which obstruct plane-polarized light, when their longer diameters (M^a) are parallel to the plane of the polarized ray.

and α-prisms { which obstruct the same beam when their longer diameters (T^a) are perpendicular to the plane of the polarized ray.

Quinine salt		Cinchonidine salt
Rhomb obtuse	115°	Rhomb 137°
„ acute	65°	„ 43°
1·57	$=M^a=$ 2·482	
1·00	$=T^a=$ 1·000	
·00001	$=P^a=$ ·00001	

	Quinine salt	Cinchonidine salt
Transmitted rays or body-colours.	1. *Polarized parallel to axis* (T^a). P^a, colourless, greenish-white, yellowish-green..	1. P^a, greenish-white, yellowish-green, dark olive-green.
	2. M^a and T^a, blood-red, *polarized in the plane of those axes*	2. M^a and T^a not observed.
	3. *Polarized perpendicular to axis* (T^a). P^a, pink, ruby-red, blood-red, sienna-brown ...	3. P^a, violet, light blue, indigo-blue.
Reflected rays or surface-colours.	1. *Polarized perpendicular to axis* (T^a). Cantharidine-green, blue-green, grass-green....	1. Brassy-yellow, golden-yellow, orange.
	2. *Polarized parallel to axis* (T^a). Dull olive-green, or vitreous and colourless on a dull black surface.	2. Dull olive, or vitreous and colourless on a dull black surface.

In the foregoing comparative Chart of the physical properties of the two salts, the axis has been assumed to coincide with a line drawn through the short diagonal of the primary rhombic crystal, which will coincide with the long diameter of the α-prism, and the plane of the breadth of the β-prism, and is therefore the T^{a} of the three rectangular crystallographic axes.

It has been compiled from the observations of Professors Stokes and Haidinger and the author. It appears to form a complete optical description of the two salts, as far as they are at present known.

Whilst in both salts the *indicative body-colours*, or those due to the more absorbed pencils (3), are only to be seen in the thinnest crystals, it is evident that the reflected rays may be seen indifferently in crystals of all thicknesses; and the author is inclined to believe that the cinchonidine salt possesses even greater tourmaline absorbent powers upon ordinary light, inasmuch as much thinner plates are required in order to obtain the indicative body-colours,—perfect absorption, and therefore total obstruction, being more early arrived at than in the case of the quinine salt.

The author's more recent analyses of the cinchonidine salts have produced the following results:—

Sulphate of Iodo-Cinchonidine.

	I.	II.	III.	IV.	Mean.
Iodine.....	39·727	39·462	39·246	38·488	39·478
Sulph. acid..	8·390	8·673	8·882	8·593	8·701
Carbon	34·936	35·73	35·792	..	35·486
Hydrogen ..	4·321	4·301	..	..	4·311
Nitrogen....	2·976	..	..	..	2·976
Oxygen	9·650	..	..	..	9·048
	100·000				100·000

which lead to the following composition:—

					Theory.	Mean of Experiments.
57 Carbon	×	6	=	342	= 35·367	35·486
40 Hydrogen	×	1	=	40	= 4·147	4·311
2 Nitrogen	×	14	=	28	= 2·884	2·976
12 Oxygen	×	8	=	96	= 10·052	9·048
3 Iodine	×	127	=	381	= 39·297	39·478
2 Sulph. acid	×	40	=	80	= 8·294	8·701
				967	100·000	100·000

which probably give the following formula:—

$$\left.\begin{matrix} C^{57}H^{38}N^{2}O^{5} \\ I^{3} \end{matrix}\right\} 2SO^{3}, HO + 5HO = 967.$$

One other remarkable difference exists between the quinine and cinchonidine salt, which is, that the optical crystals of the last salt,

if allowed to remain in the mother-solution with an excess of less than 1 per cent. of sulphuric acid, undergo a transformation, and become long, golden, silky aciculæ, radiating in beautiful globose tufts: this salt has some doubly absorbent powers also, but very feeble. When this salt is attempted to be redissolved in boiling spirit, in order to be recrystallized, it does not re-form, but the optical crystals are then produced; when the silky crystals are carefully air-dried, they retain their yellow colour, but if exposed over sulphuric acid at 62° Fahr., or if attempted to be dried at 212° Fahr., they lose 5·32 per cent. water=6 atoms, and become a dark greenish-black residue, which is a tri-hydrate and contains the following by analysis:—

	I.	II.	III.	IV.
Iodine.....	40·504	40·407	..	..
Sulph. acid....	9·064	8·324	..	..
Carbon	..	..	36·082	35·689
Hydrogen	..	36·404	36·28	36·583

numbers which very closely correspond with the following:—

					Theory.	Experiment.
57 Carbon	×	6	=	342	= 36·037	35·835
38 Hydrogen	×	1	=	38	= 4·004	4·047
2 Nitrogen	×	14	=	28	= 2·950	2·851
10 Oxygen	×	8	=	80	= 8·433	8·063
3 Iodine	×	127	=	381	= 40·147	40·455
2 Sulph. acid	×	40	=	80	= 8·429	8·699
				949	100·000	100·000

and the formula may be provisionally given as—

$$\left.\begin{matrix} C^{57} H^{38} N^2 O^5 \\ I^3 \end{matrix}\right\} 2SO^3, HO + 3HO = 949,$$

which closely corresponds with the optical salt, but contains 2 atoms less water.

If this olive-coloured residue be boiled in dilute spirit, the optical crystals deposit on cooling.

From the addition of 5·32 per cent. water to this dry residue, we find that the silky crystals contain dry residue,—

	94·678	=949=1 atom
Water	5·322	= 54=6 atoms
	100·000	1003

and we have thus the following formula for the silky salt, which corresponds most closely with the result of analysis,—

$$\left.\begin{matrix} C^{57} H^{38} N^2 O^5 \\ I^3 \end{matrix}\right\} 2SO^3 HO + 9HO = 1003,$$

as may be seen by the following comparison:—

				Theory.	Experiment.
57 Carbon	×	6	= 342	= 34·097	33·947
44 Hydrogen	×	1	= 44	= 4·386	4·423
2 Nitrogen	×	14	= 28	= 2·791	2·700
16 Oxygen	×	8	= 128	= 12·764	12·800
3 Iodine	×	127	= 381	= 37·986	37·914
2 Sulph. acid	×	40	= 80	= 7·976	8·216
			1003	100·000	100·000

giving—

Carbonic acid.....	125·22	124·472 per cent.
Water.....	39·474	39·807 „

Consequently the silky salt will be the optical salt+4 atoms of water, which, under the influence of excess of sulphuric acid and prolonged delay at 62° Fahr., are assimilated by that salt; and which additional water, on boiling in spirit, is lost, and the optical salt recrystallized on cooling.

If the temperature be not too high *at first*, the silky crystals may be produced without the appearance of the optical. And the silky crystals at 212°, or at 62° Fahr. over sulphuric acid, become the dry residue or tri-hydrate, which, when boiled in spirit, becomes the optical, by assimilating 2 atoms of water, as may be seen by comparing the three proposed formulæ:—

α. Optical.

$$\left.\begin{matrix} C^{57} H^{38} N^2 O^5 \\ I^3 \end{matrix}\right\} 2SO^3 HO + 5HO = 967$$

β. Silky Salt.

$$\left.\begin{matrix} C^{57} H^{38} N^2 O^5 \\ I^3 \end{matrix}\right\} 2SO^3 HO + 9HO = 1003.$$

γ. Dry Residue.

$$\left.\begin{matrix} C^{57} H^{38} N^2 O^5 \\ I^3 \end{matrix}\right\} 2SO^3 HO + 3HO = 949.$$

The results of the analysis of the cinchonidine salt having been so remarkably different from those of the formulæ generally adopted for the pure alkaloid, the author was induced to prepare some perfectly pure quinine, taking especial pains to exclude all cinchonidine; and having from that prepared some iodo-sulphate of quinine, to submit it to equally rigid analysis.

The results are the following:—

These optical crystals lose 2·49 per cent. water by prolonged drying at 212° in Liebig's drying apparatus.

The residue contains the following:—

	I.	II.	III.	IV.	V.
Iodine.....	30·195	30·033	30·50	31·729	31·69
Sulph. acid..	10·246	9·352	..	9·631	9·854
Carbon	41·554	..	41·34	41·456	41·048
Hydrogen ..	4·766	4·762	..	4·54	4·7375
Nitrogen....	3·711	..	..	3·380	..

Carbonic acid mean of 4 = 151·614
Water ..... = 42·326

leading to the following composition:—

		Theory.	Experimental means.
57 Carbon	= 342	= 41·606	41·3496
38 Hydrogen	= 38	= 4·623	4·7025
2 Nitrogen	= 28	= 3·409	3·5455
10 Oxygen	= 80	= 9·730	9·8024
2 Iodine	= 254	= 30·900	30·8925
2 Sulph. acid	= 80	= 9·732	9·7705
	822	100·000	100·000

which, with 2 atoms water, constitute the optical salt dried over sulphuric acid at 62° Fahr., thus:—

1 atom dry residue 822
2 atoms water 18
840

and these results may be expressed by the following formula:—

$$\left.\begin{matrix} C^{57} H^{33} N^2 O^5 \\ I^2 \end{matrix}\right\} 2SO^3 HO + 5HO = 840,$$

which appears to be the constitution of the optical salt dried at 62° Fahr. over sulphuric acid.

From this it appears that the optical salt of quinine differs in chemical atomic numbers merely in the possession of 1 atom less iodine, the cinchonidine salt having 3, the quinine salt 2 atoms iodine; but in each case 2 atoms of sulphuric acid, and 5 water, with an organic base of $C^{57} H^{33} N^2 O^5$ common to both. How this is derived from $C^{40} H^{24} N^2 O^4$ in the one case, or $C^{40} H^{24} N^2 O^2$ in the other, it is difficult to point out in the present state of the question.

Were these views correct, it might naturally be imagined that the two salts may be mutually convertible. The author has undertaken numerous experiments with this object in view; and whilst he has proved that it is possible (by boiling the quinine salt in spirit surcharged with iodine) to communicate the golden tint of the reflected ray and the blue tint of the body-colour to the crystals on their re-formation, yet this modified salt retains the crystallographic forms of the true quinine salt; whilst, by treating the cinchonidine salt by spirit and aqueous sulphurous acid, that salt is modified also, becomes fibrous in character, and assumes the red body-colour of quinine salt, yet is at once to be distinguished from the true quinine

salt even by the naked eye alone; and on redissolving these in spirit, the blue body-coloured salt again recrystallizes with its ordinary golden reflected tint. The effect of diluted sulphuric acid in converting the cinchonidine salt into the golden silky fibrous variety, is a striking distinguishing characteristic between the two alkaloids.

These facts lead to the conclusion, that the grouping of the constituent molecules in the two salts differs materially; that closely as the quinine and cinchonidine salts agree amongst themselves, they differ widely from the quinidine and cinchonine compounds.

The quinidine salt, after recrystallization, presents itself as long quadrilateral acicular prisms, having a deep ruby or garnet-red colour, with a bluish-violet or light purplish reflexion-tint; it is sometimes deposited in thin flat plates, or long, flat, acicular prisms; these, when thin, transmit a pure yellow colour, but in thicker plates it becomes reddish, with a tinge of brown.

There is scarcely any appearance of double absorption in this salt; the thicker crystals alone exhibit it, when their usual tint becomes darkened on analysis with a Nicol.

This salt requires 31 parts of boiling spirit, and 121 parts at 62° to dissolve 1; water precipitates it as a cinnamon-brown powder.

Its deep marone-coloured large aciculæ had a specific gravity of 1·7647 at 62°.

These large crystals, exposed whole to a temperature of 212°, decrepitate afterwards on exposure to the air, but dried at 212°, they do not appear to lose further water after prolonged exposure to the drying bath.

The author having supplied Dr. Sheridan Muspratt with a quantity of this salt, has been most obligingly furnished with the results of his examination; from which it will be seen that those previously obtained by the author have been confirmed.

	Herapath.				Muspratt.	
	I.	II.	III.	IV.	I.	II.
Iodine.....	39·665	39·570	39·740	39·88	39·73	39·131
Sulph. acid..	6·273	6·390	6·326	6·302	6·263	..
Carbon	32·890	32·615	32·787	..	31·998	32·311
Hydrogen ..	3·960	3·958	4·028	3·985	4·001	3·937
Nitrogen....	4·400	4·440	4·440			
Oxygen	12·812	13·027	12·697			
	100·000	100·000	100·000			

The formulæ derivable from these analyses are the following:—

				Theory.	Herapath.	Muspratt.
35 Carbon	× 6	= 210	=	32·967	32·764	32·154
25 Hydrogen	× 1	= 25	=	3·924	3·984	3·969
2 Nitrogen	× 14	= 28	=	4·395	4·44	..
10 Oxygen	× 8	= 80	=	12·559	12·743	..
2 Iodine	×127	= 254	=	39·874	39·73	39·78
1 Sulph. acid	×	40	=	6·274	6·339	6·263
		637		100·000	100·000	

and give—

$$\left.\begin{matrix}C^{35}H^{19}N^{2}O^{4}\\ I^{3}\end{matrix}\right\} 1SO^{3}HO+5HO=637,$$

which differs from Gerhardt's formula for quinidine by the loss of $C^{5}H^{5}$; but at this stage of the question it is scarcely possible to arrive at a solution of the manner in which it is produced.

The cinchonine salt differs much from all those previously described; it exists in long, acicular, quadrilateral prisms, of a deep purplish-black colour, like that of elder-berries.

Thin crystals transmit a yellow tint—pure gamboge-yellow when very thin; soon passing through a deep sherry-brown to a blood-red colour, then a deep port-wine colour, and then becoming opaque.

These crystals reflect a deep steel-blue colour when analysed with a Nicol's prism, and generally across the short diameter of the prism, which is the analogue of the α-prism of the quinine salt. The cinchonine salt possesses doubly absorbent powers, much more powerfully so than the quinidine salt, but inferior to all the others; the body-colour is deep sienna or bistre-brown.

This salt furnished the following analytical results:—

	I.	II.	III.
Iodine	50·34	50·587	50·302
Sulphuric acid ..	5·247	5·217	..
Carbon	28·156	27·57	27·37
Hydrogen.....	3·523	3·485	3·454
Nitrogen	3·306	..	..

which lead to the following composition:—

					Theory.	Experiment.
35 Carbon	× 6	=	210	=	27·7410	27·698
26 Hydrogen	× 1	=	26	=	3·4346	3·487
2 Nitrogen	× 14	=	28	=	3·7000	3·306
9 Oxygen	× 8	=	72	=	9·5103	9·8674
3 Iodine	×127	=	381	=	50·3301	50·4096
1 Sulph. acid		=	40	=	5·2840	5·232
			757		100·000	100·000

giving—

$$\left.\begin{matrix}C^{35}H^{19}N^{2}O^{2}\\ I^{3}\end{matrix}\right\} 1SO^{3}HO+6HO=757,$$

which, on comparison with the quinidine salt, will be found to possess 1 atom additional iodine, and 1 atom more water, but a deficiency of 2 atoms oxygen, the latter, apparently, in consequence of the original difference in the type of the alkaloids employed; and, like that salt, it differs in its organic base by the loss of $C^{5}H^{5}$ from

the constitution of the alkaloid originally employed, if we take the formula $C^{40} H^{24} N^2 O^2$, as given by Gerhardt, for that of cinchonine.

The cinchonine and quinidine salts further agree in containing only 1 atom sulphuric acid, whereas the quinine and cinchonidine salts contain 2 atoms.

These investigations appear to show that the alkaloids in each instance undergo some modification, but not analogous to substitution; it appears more like a splitting-up into different molecular groups, and a rearrangement of these amongst themselves, as the formulæ of the organic bases differ much from those of the original alkaloids.

All these iodo-salts possess double refractive properties.

When the acid sulphates of the mixed alkaloids, quinine, quinidine, cinchonine and cinchonidine, are dissolved in dilute spirit, and the temperature increased to 80° or 120°, treatment with tincture of iodine readily separates the quinine salt first.

Subsequent further treatment in the same manner produces the cinchonidine salt, more or less mixed with the quinine salt.

On still further treatment, the quinidine salt is formed with its well-marked characters.

The cinchonine salt is by far the most soluble in spirit; and when a large quantity of cinchonine exists, this compound will also appear along with the quinidine salt.

This test is a beautiful and ready method of proving the presence of cinchonidine in cinchonine, which would otherwise be considered pure, Brandes' test having shown the absence of quinine and quinidine. In the same way, this test is an easy method of detecting mixtures of quinine and quinidine, the optical characters of the two salts being so well marked, that no difficulties can exist in their discrimination.

It does not offer such facilities for the separation of quinine from cinchonidine; the two salts go down together, especially if large quantities of cinchonidine exist with mere traces of quinine.

For the success of this test, a small portion only is necessary: with quinine and quinidine $\frac{1}{200}$th part of a grain has furnished evidence of the two alkaloids; one grain would be abundant to detect all the alkaloids.

The foregoing method of examination has enabled the author to prove that the substance which Rosengarten, of Philadelphia, called quinidine, was really the cinchonidine of Pasteur, and the details of his cures of fever, therefore, by quinidine are rather to be ascribed to cinchonidine.

The cinchonidine of Wittstein, of Munich, is a totally different alkaloid, giving, with sulphuric acid and iodine, a salt at once to be distinguished by the eye from either of the two iodo-sulphates described, but yet possessing optically doubly absorbent powers. This salt has a deep orange-yellow colour by transmitted light merging into sienna-brown in thicker plates, which are generally flat and much imbricated in the method of crystallization, and also

derived from a rhombic prism. The reflected tints are brownish-olive, not unlike dead leaves, or brown beech-leaves. These crystals are more doubly absorbent than either the quinidine or cinchonine salt, but less powerfully optical as tourmalines than the quinine or cinchonidine compounds. When polarized, they transmit a sienna-brown body-colour if moderately thick, and thicker plates are bistre-brown, but when sufficiently thick, they are wholly impervious to plane-polarized light. The substance was not in sufficient quantity to admit of any analysis.

It is well known that quinine and quinidine, under the continued effect of heat and dilute sulphuric acid, undergo a molecular change into quinicine, which M. Pasteur has asserted to be isomeric with the original alkaloids, but hitherto no complete analysis has been made of the metamorphosed alkaloids.

The author has produced an iodo-sulphate of quinicine, but it is no longer a crystalline compound; it presents itself as a deep blood-coloured resin, very soluble in spirit and readily precipitated by water from its spirituous solution. This substance has not yet been submitted to analysis. During the production of the iodo-sulphate of quinidine a certain portion of the alkaloid becomes converted into quinicine, as may be demonstrated by the production of this resinous compound from the mother-liquid on the addition of further proportions of iodine.

Cinchonine and cinchonidine become converted into cinchonicine by similar treatment, and this amorphous alkaloid also forms a resinous iodo-sulphate; its colour is deep purple-black, and it deposits itself on spontaneous evaporation of the spirit, or on the cooling of a highly concentrated spirituous solution, in small drops, highly tenacious at 100° Fahr., but becoming solid at 60° Fahr. This compound has, in a fine state of division, a beautiful purplish-blue colour, and such a film generally forms around the edge of the vessel in which it is produced.

Cinchonicine appears to be one of the products during the manufacture of the iodo-sulphate of cinchonidine, but there is a much larger production of it during the formation of the cinchonine salt.

From the foregoing reactions, the author appears to be justified in asserting that eventually it will be found, when we know more of the rational grouping of the constituent atoms of the vegeto-alkaloids, that the construction of the formula for the cinchonidine of Pasteur will have a much greater similarity to the arrangement of the molecular groups of quinine than of cinchonine. And there is also great probability that the grouping of the atoms of cinchonine and the quinidine of Pasteur will be found to present more points of similarity; but in each case he sees no reason to doubt the existence of more oxygen in the cases of both quinine and quinidine than there is in cinchonine and cinchonidine. He also ventures to suspect that cinchonicine and quinicine will eventually be found to contain more carbon than the original alkaloid, the elements of water probably being separated by the sulphuric acid during the process of formation.

THE CHEMICAL GAZETTE.

No. CCCLXIX.—March 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Composition of Bromide of Potassium and Tellurium, and the Equivalent of Tellurium. *By* CARL RITTER VON HAUER.

THE existence of a crystallizable double compound of the bromide of potassium and tellurium was ascertained by Berzelius. This salt, however, has not been submitted to any analytical investigation, either by him or by any other chemist; nevertheless it is one of the most beautiful and best crystallizable of all known compounds of tellurium. It may be recrystallized at pleasure without undergoing any decomposition, and may therefore be prepared in a state of remarkable purity. Moreover, it may be deprived of water at a temperature but little higher than that of the water-bath, and is but slightly hygroscopic in the anhydrous state.

The author has prepared this salt in a pure state, and effected its analysis in such a way that the numbers obtained may be regarded as a check of the atomic weight of tellurium. These numbers are based upon the known atomic weights of potassium, silver, and bromine; they approach very closely to the atomic weight found by Berzelius. The author prepared large quantities of bromide of potassium and tellurium by the following process.

Fragments of the metal were placed in a flask capable of being closed, and hydrobromic acid was poured over them. A quantity of bromine was then added, the flask was closed, and left standing until the bromine had disappeared. This operation was repeated as long as uncombined portions of the metal remained in the solution. The action of the bromine takes place here almost without evolution of heat; nevertheless its combination with the tellurium goes on very rapidly, especially when the flask is frequently shaken round. By evaporating the ruby-red solution to dryness in the water-bath, dry bromide of tellurium is obtained. If the yellow mass thus obtained be left in an aqueous solution of chloride of potassium, the double compound described by Berzelius is obtained on evaporation. During the analysis of these crystals it appeared, however, that they also contained some chlorine derived from the mother-liquor. Still the result showed that potassium and tellurium are present in equal equivalents. To obtain a salt which would certainly be perfectly free from chlorine, the author then prepared

it by another method, excluding the employment of chloride of potassium.

Finely powdered metallic tellurium and bromide of potassium were placed in a flask in equivalent proportions, and water was added until the bromide of potassium was completely dissolved. Bromine was then added in small portions with frequent agitation of the flask, and the operation was continued, as already described in the preparation of the bromide of tellurium. The very finely divided metallic tellurium, which is obtained by precipitation with sulphurous acid, is well adapted for this purpose. The dark red fluid produced was heated for a long time in order to expel any excess of bromine, then filtered, as an abundant yellow sediment is always formed, and left to cool. The solubility of the compound is considerably increased by heat, so that, on the cooling of the solution concentrated by heat, a great quantity of crystals shoots out. By gradual evaporation over sulphuric acid, crystals of half an inch in diameter are obtained. They dissolve without decomposition in warm and cold water, but when much diluted tellurous acid separates. As the solution effloresces strongly during spontaneous evaporation, it is as well to smear the edges of the vessel intended for the evaporation with fat.

The crystals thus obtained were then recrystallized four times; first of all (twice) by the cooling of solutions concentrated by heat, and afterwards by spontaneous evaporation over sulphuric acid. The last formed salt was dried at 248° F., and left to cool over sulphuric acid.

Since the salt, as already stated, contains potassium and tellurium in equivalent proportions, and is therefore composed, in the anhydrous state, in accordance with the formula

$$Ka\,Br + Te\,Br^2,$$

the equivalent of tellurium could be calculated from the amount of bromine contained in it. The determination was effected by dissolving a weighed quantity of the anhydrous salt in dilute nitric acid, and precipitating it by means of a solution of pure nitrate of silver. Five experiments gave the following results, taking silver =108·1, and bromine =80:—

2000	grains of the substance		gave	69·9460	per cent.	of bromine.
6668	„	„	„	69·8443	„	„ „
2934	„	„	„	69·9113	„	„ „
3697	„	„	„	70·0163	„	„ „
1000	„	„	„	69·9001	„	„ „
			Average..	69·9236	per cent.	of bromine.

The salt therefore consists in 100 parts of

69·9236 bromine,
30·0764 potassium and tellurium.

Assuming the equivalent of potassium to be =39·2, the equivalent of tellurium is found from this per-centage composition to be =64·03, or as a second place of decimals is hardly worth adding, in round

numbers =64 (800, if O=100). Berzelius, who determined the equivalent of tellurium by oxidizing the metal by means of nitric acid, and weighing the tellurous acid produced, found, in his first investigation in the year 1813, that 100 parts of metal gave 124·8 of tellurous acid, and in a second experiment, that 201·5 parts of fused tellurate of lead gave 157 parts of sulphate of lead; from this he calculated the equivalent of tellurium =806·48 to 819 (64·5 to 65·5, with H=1).

In the year 1833, Berzelius repeated the experiments to determine the equivalent by oxidation with nitric acid, and found, in these experiments, that 100 parts of metal took up 24·9116, 24·9443, 24·9456 of oxygen; from the average of the two last experiments he calculated the equivalent of tellurium =801·76 (64·14, with H=1).

This number, therefore, only differs by 0·14 from that obtained by the author in a totally different way. The round number 64 has also been already adopted by many chemists, especially by Gmelin in his 'Manual,' although it had not hitherto been ascertained experimentally.

To determine the constitution of the salt in the crystallized state, it remained to ascertain the quantity of water of crystallization. These experiments gave the following results:—

0·935	grain of crystals lost by heat	7·27	per cent.	of	water.
1·346	„ „ „	7·42	„	„	
0·987	„ „ in the water-bath	7·29	„	„	
	Average..	7·32	per cent.	of	water.

Finally, the quantity of potassium was determined as a check. If the crystals be more strongly heated after the expulsion of the water, the greater part of the bromide of tellurium is driven off in yellow fumes, whilst bromide of potassium remains. Nevertheless the bromide of tellurium cannot be entirely got rid of in this way, as a small quantity becomes converted into tellurous acid by the access of atmospheric air. For the determination of the potassium, therefore, the heat must not be so great as to cause the fusion of the residuary mass, as the remaining quantity of tellurous acid might form tellurite of potash. On lixiviation with water, the bromide of potassium dissolves, whilst the small quantity of anhydrous tellurous acid remains undissolved. It is filtered, and the filtrate when evaporated to dryness, gives the quantity of bromide of potassium contained in the salt.

Treated in this way, 0·935 gr. of crystals gave 0·294 gr. of bromide of potassium =10·34 per cent. of potassium. From this the formula of the crystallized salt is—

$$Ka\,Br + Te\,Br^2 + 3HO.$$

			Calculated.		Found.
1	equivalent	Ka	39·2	10·58	10·54
1	„	Te	64	17·28	17·51
3	„	Br	240	64·82	64·83
3	„	HO	27	7·29	7·32

When heated, the salt loses its water of crystallization without fusing; when more strongly heated, bromide of tellurium is also evolved. The dehydrated salt is of an orange-yellow colour, which becomes somewhat darker every time it is heated, but lighter again on cooling. The crystals are opake, of a dark red colour, and have a brilliant surface-lustre. In dry air, they effloresce superficially, and become yellow.—*Sitzungsber. der Akad. der Wiss. zu Wien.* xxv. p. 135.

On some Compounds of Acetamide. *By* A. Strecker.

Muriate of Acetamide, $2(C^4 H^5 NO^2) + HCl$.—This is produced—1. when oxychloride of phosphorus is added to acetamide which has been fused by a gentle heat. The two bodies set into a solid mass, without any evolution of muriatic acid. Anhydrous æther does not dissolve the compound. It dissolves in absolute alcohol, and on cooling, or on the addition of æther, the compound separates with the composition above given. The compound of acetamide with oxychloride of phosphorus evidently decomposes, when in contact with alcohol, into phosphoric æther and muriatic acid, of which the latter combines with the acetamide. 2. It is still more easily obtained by passing muriatic acid gas into a solution of acetamide in æther and alcohol. The gas is only passed upon the surface of the solution, which is strongly refrigerated.

The crystals may be washed with æther, and purified by recrystallization from alcohol. Æther also precipitates it from this solution. The alcoholic solution gives no precipitate with perchloride of platinum; in course of time chloride of platinum and ammonium separates, and an odour of acetic æther is perceived. The alcoholic solution deposits muriate of ammonia in time.

Nitrate of acetamide, $C^4 H^5 NO^2 + HO, NO^5$, is formed when cold concentrated nitric acid is brought into contact with acetamide. Colourless crystals, which explode when heated.

Hydrargyracetamide, $C^4 H^4 HgNO^2$.—Oxide of mercury is taken up by solution of acetamide, which when gently heated is completely saturated therewith. By evaporation *in vacuo*, colourless crystalline crusts are obtained. Their solution gives no precipitate with potash, but when boiled furnishes white flakes. Ammonia immediately produces a yellowish turbidity, which increases considerably by boiling. Zinc precipitates the mercury from the solution, and the acetamide becomes free from metal again; the zinc does not enter into combination in place of the mercury, but separates in flakes of hydrated oxide.

Argyracetamide.—Freshly precipitated oxide of silver dissolves in aqueous acetamide. When evaporated, argyracetamide remains.

Metamorphoses.—Acetamide, when heated with water, is readliy converted into acetic acid and ammonia by the action of acids and strong bases.

When perfectly dry muriate of acetamide is sealed up with dry muriatic acid in a glass tube and heated to 356°–392° F., or when

acetamide is heated in a stream of dry muriatic acid, a colourless fluid and a solid crystalline body are formed and distilled over; a solid, hardly volatile body remains in the retort.

The fluid distillate contains chloride of acetyle, and perhaps acetonitrile (cyanide of methyle). The solid body in the distillate was partly muriate of acetamide which had passed over unchanged; æther extracted from it a body which was deposited on evaporation in hard crystalline granules. These were readily soluble in water, æther and alcohol, readily fusible and volatilizable even *in vacuo*. Its analysis gave the composition

$$C^{12} H^{12} N^2 O^6 = \underset{\text{Acetamide.}}{C^4 H^5 NO^2} + \underset{\text{Diacetamide.}}{C^8 H^7 NO^4}.$$

If muriatic acid gas be passed into the ætherial solution of this compound, crystals of muriate of acetamide separate. This body is therefore a compound or mixture of acetamide with the new body

Diacetamide, $C^8 H^7 NO^4$, which the ætherial solution deposits in long acicular crystals, as soon as the æther is evaporated. These crystals are readily soluble in water, æther and alcohol. Perchloride of platinum produces no alteration in the solution in the cold; when boiled, chloride of platinum and ammonium separates. When boiled with acids, this body is decomposed into acetic acid and ammonia. Analysis:—

C	47·7	8=48	47·5
H	6 9	7 11	6·9
N	..	14 14	13·9
O	..	32 32	31·7

The above-mentioned solid residue in the retort consists of muriate of ammonia and the muriate of a new, strong base. The latter is extracted with alcohol and purified from muriate of ammonia by recrystallization from æther and alcohol. This salt of the new base is the author's

Muriate of Acediamine, $C^4 H^6 N^2$, HCl.—This salt gives no precipitate on the addition of perchloride of platinum, but when the solution is evaporated, furnishes tolerably large, hard, yellowish-red crystals of a platinum double salt, which is readily soluble in water, less soluble in alcohol, and insoluble in æther and alcohol.

The *muriate of acediamine* and *chloride of platinum* has the composition $C^4 H^6 N^2$, $HC + PtCl^2$. It contains 37·3 and 37·2 per cent. of platinum. The formula requires 37·4 per cent.

Sulphate of Acediamine, $C^4 H^6 N^2$, HO, SO^3, is obtained by mutual decomposition, when sulphate of silver is brought in contact with the muriate. The solution filtered from the chloride of silver, furnishes crystals after evaporation in the water-bath. It contains 37·3 per cent. of sulphuric acid. The formula requires 37·2 per cent. The base could not be obtained in a free state, because, as soon as it is liberated from its salts, it becomes decomposed. When the author purposely decomposed the sulphate by boiling with baryta water, acetic acid and ammonia were formed in accordance with the following equation:—

$$C^4 H^6 N^2 + 4HO = C^4 H^4 O^4 + 2NH^3.$$

The principal products of the decomposition of acetamide by muriatic acid are consequently diacetamide, acediamine, muriate of ammonia and acetic acid, a small quantity of perchloride of acetyle, and probably acetonitrile. These products are the results of different decompositions, which may be expressed by the following equations:—

$$\underset{\text{Acetamide.}}{2(C^4 H^5 NO^2)} + HCl = \underset{\text{Diacetamide.}}{C^8 H^7 NO^4} + NH^4Cl.$$

$$\underset{\text{Acetamide.}}{2(C^4 H^5 NO^2)} + HCl = \underset{\text{Muriate of acediamine.}}{C^4 H^6 N^2, HCl} + \underset{\text{Acetic acid.}}{C^4 H^4 O^4}.$$

$$\underset{\text{Acetamide.}}{C^4 H^5 NO^2} + 2HCl = \underset{\text{Perchloride of acetyle.}}{C^4 H^3 O^2 Cl} + NH^4 Cl.$$

$$\underset{\text{Acetamide.}}{C^4 H^5 NO^2} = \underset{\text{Acetonitrile.}}{C^4 H^3 N} + 2HO.$$

By the water set free in consequence of the last mode of decomposition, a certain quantity of acetamide will be decomposed into acetic acid and ammonia.

Gerhardt and Laurent formerly distinguished six classes of amides, but this number has since been increased. All the amides hitherto known, however, may be derived from the neutral or acid ammoniacal salts of mono- or bibasic acids by the elimination of water.

Acediamine is the first amide which divides into 1 equiv. acid and 2 equivs. ammonia by the reception of water; it would consequently be derivable from a basic ammoniacal salt, if such a thing existed. The author has already found that other allied amides, such as benzamide, behave similarly when treated with dry muriatic acid, and many bases with N^2 which occur in nature may have a similar constitution.

The three amides, acetamide, diacetamine and acediamine, are all produced from acetic acid and ammonia by the elimination of the elements of water. The relations in which their chemical characters stand to those of their original material are as follows:—

Acetamide, $\left.\begin{matrix} C^4 H^3 O^2 \\ H \\ H \end{matrix}\right\}$ N, which may be referred to the type of ammonia, and has been formed from 1 equiv. of acetic acid and 1 equiv. of ammonia, still retains the faculty of ammonia of uniting with acids.

Diacetamide, $\left.\begin{matrix} C^4 H^3 O^2 \\ C^4 H^3 O^2 \\ H \end{matrix}\right\}$ N, which has been formed from 2 equivs of acetic acid and 1 equiv. of ammonia, no longer has the faculty of forming salts with acids.

Acediamine, $C^4 H^6 N^2$, is produced from 2 equivs. of ammonia with 1 equiv. of acetic acid; it has the character of an organic base. Acediamine is derived from acetamide in the same way as acetamide from acetic acid, or æthylamine from alcohol:—

$$C^4H^5NO^2 + NH^3 = C^4H^6N^2 + 2HO.$$
Acetamide. Acediamine.

$$C^4H^6O^2 + NH^3 = C^4H^7N + 2HO.$$
Alcohol. Æthylamine.

These relations are of course quite independent of opinions as to the constitution of these compounds, and room is left for more or less favoured views of the constitution.

The author, in conclusion, recapitulates the combinations according to which, following one or the other system, we might construe these bodies in different ways, and without attaching any further importance to such attempts, he shows that this might be done variously as follows. We might derive acetamide from the type water $\left.\begin{matrix} C^4H^4N \\ H \end{matrix}\right\} O^2$, and acediamine from the type ammonia by the displacement therein of 1 equiv. of hydrogen by the radical C^4H^4N, thus $\left.\begin{matrix} C^4H^4N \\ H \\ H \end{matrix}\right\} N$. The radical C^4H^4N might also be derived from æthyle, C^4H^5, by the displacement of hydrogen by nitrogen.

We might however asssume in acediamine a radical C^4H^3 equivalent to 3 equivs. hydrogen, deriving the base from the type $\left.\begin{matrix} H^3 \\ H^3 \end{matrix}\right\} N^2$, and consequently writing its rational formula $\left.\begin{matrix} C^4H^3 \\ H^3 \end{matrix}\right\} N^2$ Others would perhaps rather regard acediamine as an acetonitrile conjugated with ammonia, $C^4H^3N + NH^3$.—Liebig's *Ann.*, ciii. p. 321.

On the Amides of Phosphoric Acid. *By* Dr. Hugo Schiff.

Perfectly dry ammoniacal gas acts violently upon anhydrous phosphoric acid. If it be allowed to cool in the current of gas, there remains a mixture of phosphaminic acid and phosphaminate of ammonia, contaminated with red amorphous phosphorus.

Phosphaminic acid, $\left.\begin{matrix} N(HPO^2) \\ H \end{matrix}\right\} O^2$, belongs to the type $\left.\begin{matrix} NH^4 \\ H \end{matrix}\right\} O^2$; it is the aminic acid corresponding therewith, triatomic phosphoryle PO^2 taking the place of H^3 in the ammonium. Its mode of production is

$$\left.\begin{matrix} PO^2 \\ PO^2 \end{matrix}\right\} O^6 + 2NH^3 = 2\left.\begin{matrix} N(HPO^2) \\ H \end{matrix}\right\} O^2 + 2HO.$$

It is a semisolid, non-crystalline mass, readily soluble in alcohol and water. When heated, it gives phosphoric acid and ammonia.

The salts of phosphaminic acid are obtained by double decomposition. The alkaline salts are soluble, as are also a series of others, in which hydrogen is replaced by ammonium containing metal. The metallic salts form flocculent crystalline precipitates which are insoluble. When heated, they evolve ammonia and leave phosphates. The phosphaminates are far less soluble in acid fluids than the phosphates.

The iron salt is nearly insoluble even in tolerably concentrated sulphuric acid. Phosphaminic acid can only be converted into

ordinary phosphoric acid by repeated evaporation with the occasional addition of chlorate of potash.

The *Ammoniacal Salt* is obtained by dissolving the crude product in water, neutralizing it completely, filtering, and evaporating it. The salt remains in a radiately crystalline form, but contains intermixed phosphate of ammonia.

The *Lime-salt*, $\left.\begin{matrix}N(HPO^2)\\Ca\end{matrix}\right\}O^2$, forms a white precipitate, which, when dried at 230° F., is anhydrous. It is insoluble in ammonia, and contains 20·1 per cent. of calcium and 32·5 per cent. of phosphorus (calculated 20·3 and 32·0 per cent.).

The *Baryta-salt*, $\left.\begin{matrix}N(HPO^2)\\Ba\end{matrix}\right\}O^2$, containing 47·1 per cent. of barium and 21·2 per cent. of phosphorus, is exactly similar to the lime-salt.

The *Strontia-* and *Magnesia-salts* are similar white precipitates, insoluble in ammonia.

The *Iron-salt*, $\left.\begin{matrix}N(HPO^2)\\Fe\end{matrix}\right\}O^2$, is a white, voluminous, flocculent, crystalline precipitate, which, as already stated, is precipitated from fluid strongly acidified with sulphuric acid. It dissolves completely in ammonia. Analysis gave:—

N	..	..	..	1	=14	11·2
H	..	..	..	1	1	0·8
Fe	22·62	..	22·5	1	28	22·5
P	24·95	..	..	1	31·4	25·2
O	..	..	..	4	32	25·8
HO	14·8	14·5	..	2	18	14·5

Ferrammonium-salt, $\left.\begin{matrix}NHPO^2\\NH^3Fe\end{matrix}\right\}O^2$.—The iron-salt dissolves in ammonia with a deep purple-red colour; the solution, when evaporated at a gentle heat, leaves the salt in the form of an amorphous ruby-red mass, which, on drying, separates from the vessel in columnar fragments. The solution of the salt is neutral; with potash it gives a precipitate of oxide of iron only when boiled; ferrocyanide of potassium gives no precipitate; on the addition of a drop of acid, the solution becomes deep blue, but only deposits prussian blue when boiled. The salt dried at 176° — 194° F., is anhydrous. It contains 23·1 of iron (calculated 22·7).

The *Cobalt-salt* is a beautiful rose-coloured precipitate, which dissolves with the same colour in ammonia. When fused with hydrate of potash, it furnishes a deep blue enamel, from which hydrated oxide of cobalt only separates when water is poured over it. The salt acquires a similar blue colour when solution of potash is poured over it; the colour of the hydrated oxide only appears on boiling.

The *Nickel-salt*, $\left.\begin{matrix}NHPO^2\\Ni\end{matrix}\right\}O^2$.—A greenish-white precipitate, which dissolves in ammonia with an azure-blue colour; when heated,

the solution soon becomes green, and on evaporation leaves an amorphous sap-green salt, probably $NH(NH^3Ni)PO^4$. Analysis:—

Nickel	23·5	23·5
Phosphorus	24·9	24·6

Solution of phosphaminate of ammonia also gives voluminous precipitates with other metallic salts; these are pale blue with copper salts, dingy green with salts of chromium, and white with salts of mercury, silver, zinc, lead, and manganese. With the exception of the lead and manganese salts, they are soluble in ammonia, and probably constitute compounds analogous to the ferrammonium salt.

Anhydrous phosphoric acid, when saturated as completely as possible with ammoniacal gas, and heated in a current of dry ammoniacal gas, is decomposed with effervescence. Water afterwards dissolves the glassy phosphoric acid produced, and there remains *Phospham* (the so-called phosphuretted nitrogen), PN^2H, thus

$$\left.\begin{matrix} N(H, PO^2) \\ NH^4 \end{matrix}\right\} O^2 - 4HO = \left.\begin{matrix} NHP \\ N \end{matrix}\right\}.$$

Phospham is consequently the nitrile of phosphaminic acid.

Biphosphamide, $N^2 \left\{\begin{matrix} PO^2 \\ H^3 \end{matrix}\right.$, could not be prepared from the ammoniacal salt.

By an enumeration of the properties of Gladstone's deutazophosphoric acid, the author shows it to be probable that this is identical with the phosphaminic acid here described.

Aniline also acts very violently upon anhydrous phosphoric acid. The product of the action may probably contain phenylophosphaminic acid, $\left.\begin{matrix} N, C^6H^5, PO^2 \\ H \end{matrix}\right\} O^2$ (phosphanilic acid).

Of the acid amides of inorganic acids, therefore, we now know the four following aminic acids:—

Sulphaminic acid	$\left.\begin{matrix} NH^2, S^2O^4 \\ H \end{matrix}\right\} O^2$,	
Thionaminic acid	$\left.\begin{matrix} NH^2, S^2O^2 \\ H \end{matrix}\right\} O^2$,	
Phosphaminic acid	$\left.\begin{matrix} NH, PO^2 \\ H \end{matrix}\right\} O^2$,	and
Osmiamic acid	$\left.\begin{matrix} N, Os^2O^4 \\ H \end{matrix}\right\} O^2$	(Osman-Osmic acid).

Liebig's *Annalen*, ciii. p. 168.

Remarks on M. von Babo's *Paper* "*On some Decompositions of Cinchonine.*" *By* C. Greville Williams*.

In the 'Chemical Gazette' for February 1st, there appeared a translation of a paper by M. von Babo†, in which he investigates the action of sulphate of methyle on chinoline. M. von Babo states, that he was led from his experiments on the electrolysis of cinchonine, to conclude that base to be a copulated compound of chinoline with

* Communicated by the Author. † Journ. für Prakt. Chemie, lxxii. p. 73.

a methyle or formyle compound. Many years ago Hofmann enunciated similar ideas. M. von Babo does not appear to be aware of the researches which have recently been made upon cinchonine and chinoline. His experiments on the action of methyle-sulphuric æther on chinoline are analogous to mine with methyle-hydriodic æther; and the resulting products appear to be absolutely the same. M. von Babo treats chinoline first with methyle-sulphuric æther, and the resulting product with caustic alkalies. I treated chinoline first with methyle-hydriodic æther, and then with oxide of silver. In my paper* I state that "the decompositions of the hydriodate (of methyle-chinoline) almost exactly resemble those of the æthyle base; and as the atomic weight of the latter, being higher, gave it an advantage for experiment, I selected it for the purpose." M. von Babo, by acting with caustic potash or baryta on the product obtained as above, found that "a gaseous body was liberated which violently excited sneezing and flow of tears." In my paper I state, "When the solution of hydriodate of æthyle-chinoline is heated on the water-bath with excess of oxide of silver, a volatile product is evolved acting strongly on the eyes." M. von Babo obtains by the action of potash a fluid at first red, then becoming green, and then violet. My paper states the solution of the base liberated by oxide of silver to be "of a splendid crimson colour, the sides of the basin where the liquid has dried becoming a brilliant emerald-green, passing into a blue of great beauty and intensity."

The analogy between the results of M. von Babo and mine become still more striking, if that portion of his paper where he describes the properties of the solution (after separation of the alkaline base) be compared with mine where I avoid the presence of any inorganic base in solution by acting with sulphate of silver on iodide of æthyle-chinoline†. In fact, if the upper part of p. 51 of the last Number of the Chemical Gazette be compared with the upper part of p. 285 of the previous volume, the resemblance between his description of the coloured reactions which ensue and mine is startling. For example, after evaporating the solution of the base (obtained from the sulphate) to dryness and redissolving in water, he obtains a liquid having the following properties:—"It dissolves in water with a dark red colour. The aqueous solution evaporated to dryness yields a violet amorphous mass of brilliant cupreous lustre, which on standing in the air assumes a beautiful green colour." These reactions of the free base agree with the solution of the base examined by me, but still more with my description of the coloured reactions of the sulphate, which was as follows:—

"If hot solutions of sulphate of silver and hydriodate of æthyle-chinoline are mixed, double decomposition ensues, without any further action taking place, the solution of sulphate of æthyle-chinoline remaining colourless, and the iodide of silver separated being

* Trans. Royal Soc. Edinburgh, vol. xxi. part 3, and Chem. Gaz. 1856, p. 283.

† It appears that the solution of the free base, and also the sulphate, afford similar coloured reactions by the oxidizing influence of the air.

of the normal tint; but if it be attempted to concentrate the solution by evaporation on the water-bath, it undergoes a curious metamorphosis; the sides of the dish where the solution has dried become a deep pure blue, but as the evaporation proceeds, the solution becomes crimson, and when dry, the mass is so deep in tint as to be nearly black. The dry substance has a slight coppery lustre, like that which indigo possesses when rubbed."

Other portions of M. von Babo's paper resemble mine in a no less remarkable manner. I had even gone so far as to make an approximative determination of the atomic weight of the new base, the number yielded being 212·2. M. von Babo's analyses "seem to point to $C^{26}\,H^{18}\,N^{2}\,O^{4}$;" this formula (which will probably require modification) would indicate an atomic weight of 234.

I should not have taken so much trouble to show the priority of my investigation, were it not that I have by no means relinquished the subject, in fact that portion of my paper previously quoted from concludes with the following sentence:—"I have therefore promised myself to examine the matter more fully, when the other investigations with which I am now occupied are concluded." It may be stated in confirmation of this, that I obtained a few months ago a second quantity of 100 ounces of cinchonine for the purpose.

Although confident that M. von Babo's silence with regard to my experiments has merely arisen from his not having seen any record of them, I may mention that they were quoted (I think *in extenso*) in one of the German chemical journals.

The coloured reactions of the products of the decomposition of chinoline acquire interest from the fact that most nitrile bases yield analogous results, it is therefore not too much to hope that the vast quantities of the pyridine and chinoline series present in coal-tar may eventually be applied to practical purposes.

Dr. Gregory* has even thrown out the suggestion that the products obtained by me from chinoline may be related to pittacal. Without expressing any opinion upon that point, it seems clear that the tar of wood and coal is the raw material to which the decorative arts will sooner or later be indebted for some of their most beautiful effects. The pittacal of Reichenbach would unquestionably be a valuable dye-stuff, if procurable in sufficient quantity and at a sufficiently low price. I am at present occupied in endeavouring to solve the chemical portion of this problem.

To conclude, I cannot accept M. von Babo's name for my base, because its nature not yet being known, any nomenclature on the subject would be premature.

Note on the Action of Hydrocyanate of Ammonia upon Alloxane. By A. Rosing *and* L. Schischkoff.

Under the influence of oxidizing agents uric acid is converted into urea and alloxane:—

$$C^{10}\,O^{6}\,N^{4}\,H^{4}+O^{2}+H^{2}\,O^{2}=C^{8}\,O^{8}\,N^{2}\,H^{2}+C^{2}\,H^{4}\,N^{2}\,O^{2}.$$

* Handbook of Organic Chemistry (Edit. 1856), p. 471.

On comparing the composition of alloxane with that of uric acid, the two bodies are found to differ by O^2, which are replaced by Cy NH^2 to form uric acid,—

$$C^8 O^6 N^2 H^2 . O^2 = \text{alloxane},$$
$$C^8 O^6 N^2 H^2 . Cy\,NH^2 = \text{uric acid}.$$

The object of the present investigation is the transformation of alloxane into uric acid, by replacing O^2 by Cy NH^2, and to effect this the authors tried the action of hydrocyanate of ammonia upon alloxane, hoping to effect an elimination of water at the expense of the oxygen of the alloxane, at the same time that the residue of the hydrocyanate of ammonia would replace the O^2 under the form of water,—

$$C^8 O^6 N^2 H^2 O^2 + Cy\,NH^3 = H^2 O^2 + C^8 O^6 N^2 H^2 . Cy\,NH^2.$$

They were led to the choice of this reagent by the properties of alloxane, which are to yield readily 2 atoms of oxygen (alloxantine, dialuric acid), and to become converted under the influence of free ammonia into mecomelic acid, by giving up 2 equivs. of water,—

$$C^8 O^8 N^2 H^2 + 2NH^3 = 2H^2 O^2 + C^8 O^4 N^4 H^4.$$

But in this they did not succeed; in place of uric acid, they obtained a body apparently of a very complex nature, and the composition of which could not be determined with certainty by the reactions which the authors have hitherto been able to investigate.

A solution of alloxane poured in small portions into a solution of hydrocyanate of ammonia, gives rise almost immediately to an abundant white precipitate, which is seen under the microscope to consist of very small crystals loosely interlaced. The precipitate is insoluble in cold water, is almost completely decomposed by boiling water, and only recrystallizes in very minute quantities in the form of a powder endowed with satin-like lustre. Potash and ammonia readily dissolve it, but the precipitate cannot be regenerated from this solution.

When triturated with slaked lime, it evolves a considerable quantity of ammonia. The analysis gave the following results, corresponding with the formula $C^{30} H^{26} N^{14} O^{30}$:—

	I.	II.	III.	IV.	Calculated.
C	27·68	27·48	27·26	27·00	28·05
H	4·37	4·13	4·01	3·96	4·05
N	30·29	30·08	..	..	30·52
O	..	..	..	..	37·38

When boiled with solution of caustic potash until the ammonia is entirely expelled, the precipitate gives origin to oxalate of potash. Two quantitative determinations showed that 100 parts of the precipitate contain 17·5 of carbon which is converted into oxalate under the above-mentioned conditions; this is $\frac{2}{3}$rds of the total carbon of the precipitate. As alloxane does not furnish oxalic acid under these circumstances, it is probable that the precipitate contains the oxalic group; the authors therefore call it *oxalane*.

If alloxane be represented as an amide derived from carbonic and

mesoxalic acids, oxalane may be expressed as an analogous amide containing the oxalic group in addition to the carbonic and mesoxalic groups:—

$$\text{Alloxane} = N^2 \left\{ \begin{matrix} C^6 O^6 \\ C^2 O^2 \\ H^2 \end{matrix} \right. \qquad \text{Oxalane} = N^{14} \left\{ \begin{matrix} (C^6 O^6)^2 \\ (C^4 O^3)^3 \\ (C^2 O^4)^3 \\ H^{26} \end{matrix} \right.$$

The authors suppose, that in the reaction which takes place between alloxane and hydrocyanate of ammonia, the latter acts only by its ammonia, as the proportion of carbon and oxygen remains as in alloxane; to ascertain how much ammonia is contained in oxalane in a saline state, it was treated with concentrated sulphuric acid, which dissolved it completely, and on adding a large quantity of water, a silky precipitate was found, which reminds one of uric acid under the same circumstances.

This precipitate dissolves in a very large quantity of water with the aid of heat, and is again thrown down on cooling; its analysis gave the following results, corresponding with the formula $C^{22} H^{18} N^{12} O^{26}$:—

	I.	II.	III.	Calculation.
C	25·25	25·67	24·81	25·09
H	3·60	3·77	3·66	3·42
N	31·8	31·3	..	31·93
O	..	..	..	39·55

This formula shows that in oxalane there are not more than 2 equivs. of nitrogen in the form of ammonia, the remainder being probably in the form of amide.

The mother-liquors of the dilute sulphuric acid from which the body was precipitated, deposited large prismatic crystals after some time; their quantity is always proportionably very small. Their analysis gave numbers corresponding with the formula $C^{16} H^{10} N^4 O^{18}$:—

		Calculated.
C	30·9	31·37
H	3·27	3·26
N	17·15	17·11
O	..	48·26

This substance thus presents the composition of dialuric acid, plus 3 equivs. of water, but its properties are quite different.

On boiling the precipitate $C^{22} H^{18} N^{12} O^{26}$ with caustic potash, of 22 equivs. of carbon, 16 give rise to the formation of oxalic acid. It is also observable that there is a certain relation between the carbon and nitrogen of this latter body, and those of oxalane; thus—

$$2 \times 30 = 2 \times 22 + 16$$
$$2 \times 14 = 2 \times 12 + 4$$

By boiling oxalane for a long time with a large quantity of water it is dissolved at last; the liquid when evaporated gives a crystalline mass with an acid reaction; it is dissolved again in hot water, and that which first crystallizes is collected. The examination of these

crystals showed them to be oxalurate of ammonia, whilst the mother-liquor contained neutral and acid oxalates of ammonia.

$$\underbrace{C^{30}H^{26}N^{14}O^{30}}_{\text{Oxalane.}}+13H^2O^2=\underbrace{C^6O^8N^2H^4NH^3}_{\text{Oxalurate of ammonia.}}+\underbrace{5C^4O^8H^2N^2H^5}_{\text{Neutral oxalate.}}+\underbrace{C^4O^8H^2NH^3}_{\text{Acid oxalate.}}$$

This method of preparing oxaluric acid appears to be preferable to the old one.—*Comptes Rendus*, January 11, 1858, p. 105.

On some New Products of Decomposition of Bodies of the Uric Acid Group. *By* H. Hlasiwetz.

When 1 part of parabanic acid is enclosed with 3 to 4 parts of brown iodide of æthyle, such as is produced by the spontaneous decomposition of iodide of æthyle in the light and with 2 parts of alcohol of spec. grav. 0·833 in a tube of 2½ feet in length, and heated to 212° F. for 6 to 7 days, the fluid no longer deposits any parabanic acid in shining laminæ. At the conclusion of the experiment granular crystals are found at the bottom of the tube. After the excess of iodide of æthyle has been distilled off, and the liquid left to spontaneous evaporation, it furnishes another body, which, on recrystallization from alcohol, forms splendid, green, prismatic crystals, often of very large size, which possess the lustre of the wing-cases of beetles. By transmitted light and at the edges they appear brown. They exhibit the most beautiful lustre when they lie under water.

They are readily soluble in alcohol and ordinary æther, but cold water dissolves very little of them. When heated, they fuse into oily drops, and the fluid becomes brown. At a boiling heat, a large quantity of iodine is evolved in violet fumes; the fluid, which was at first dark, gradually becomes paler, and at last colourless, with an acid reaction. When evaporated to dryness, the residue contains iodide of ammonium and oxalic acid. Water containing iodide of potassium dissolves no more than pure water. Solution of potash when heated dissolves the substance without acquiring any colour. An ammoniacal odour is then observed besides the saffron-like odour of the combined iodine. Alcoholic solution of ammonia decomposes the solution of the body, with deposition of a white crystalline powder, which exhibits all the properties of oxamide, whilst the fluid gradually becomes colourless. It then contains only iodide of ammonium, and when carefully evaporated furnishes that salt in cubic crystals, which acquire a somewhat yellow colour in the air, and are very deliquescent.

The decomposition might be expressed by

$$2(C^{18}H^{17}NO^{10}I^2)+6(NH^4O)=3\underbrace{(C^4H^4N^2O^4)}_{\text{Oxamide.}}+6\underbrace{(C^4H^6O^2)}_{\text{Alcohol.}}+2(NH^4I)+2HO+I^2.$$

Iodide of ammonium.

Nitric acid immediately deprives the crystals of their green lustre, and gives them a graphite-like colour. When heated a violent

reaction takes place, in consequence of which they are dissolved with a fine red colour, and with evolution of red fumes. By the further application of heat the fluid again becomes colourless, and after it is diluted and neutralized with ammonia, oxalic acid may be detected in it. Muriatic acid has a similar action. When heated upon platinum the body fuses very readily, then evolves vapours of iodine, and leaves a colourless residue. When further heated this also emits some more vapour of iodine, and then disappears completely without any further odour. By agitating the alcoholic solution with silver and mercury, iodine is extracted from the substance. Analysis gave—

		Calculated. $C^{18}H^{16}NO^{10}I^2$	or $C^{18}H^{17}NO^{10}I^2$.	Mean of experiments.
C^{18}	108	22·90	22·85	22·88
H^{16}	16	3·39	3·58	3·63
N	14	2·96	2·95	2·55
O^{10}	80	16·98	16·91	17·35
I^2	253·6	53·77	53·66	53·64

The first granular crystals are the quadroxalate of ammonia of Graham, together with oxalic acid. An iodide in brassy yellow crystals, which is formed as a subsidiary product, could not be analysed.

Iodide of æthyle could not be introduced into alloxane in place of hydrogen, in experiments made by Dr. Bukeisen.

In connexion with these experiments, the author exposed uric acid for three days to a temperature of 320° to 374° F. in Frankland's digester. A yellow solution was thus formed; it was filtered and evaporated. After about half the water had been driven off, the fluid became turbid, acquired an orange-yellow film, and on cooling deposited an abundance of a yellow, flocculent, gelatinous, uncrystalline substance.

This is very voluminous, stops the filter like freshly precipitated hydrated oxide of iron, contracts greatly when dried, and furnishes a yellow, light powder, with a brownish tinge. When dried at 248° F., this substance has the same composition as mycomelic acid, $C^8H^4N^4O^4$. Alloxantine, treated in the same manner, is converted, as Dr. Bukeisen has found, into oxalate of ammonia and carbonic acid.

$$C^{16}H^{10}N^4O^{20}+4HO=C^4(N^2H^8)O^8+2NH^3+2C^2O^4+4C^2O^2.$$

Alloxantine. Oxalate of ammonia.

Liebig's *Annalen*, ciii. p. 200.

On the Use of Hydrate of Alumina in the Analysis of Vegetable Constituents. By Prof. Rochleder.

Hydrate of alumina precipitates certain colouring matters from their solutions, but there are others which it does not precipitate, and hence it affords a convenient means of separating many substances, especially the constituents of plants. Towards several other organic substances it exhibits the same deportment. Hydrate of

alumina has many advantages over hydrated oxide of lead; for the latter can scarcely ever be obtained pure, while, by the use of sulphide of ammonium, nothing is easier than the preparation of a pure hydrate of alumina.

In many cases a solution of alum may be directly added to the aqueous extract of a plant, and the organic substance precipitated in combination with the alumina by the addition of ammonia. The author adduces an example. An aqueous decoction of chestnut bark, mixed with solution of alum and ammonia in excess, gives a fawn-coloured precipitate, and the filtrate has a pale wine-colour. On neutralizing the latter with acetic acid, and evaporating to dryness, a residue remains, consisting of sulphate of potash and ammonia, and small quantities of acetate of ammonia. The æsculine is all contained in this residue. By boiling with a little strong alcohol, and filtering, the æsculine is separated from the sulphates, and crystallizes on evaporation of the small quantity of alcohol. By pressing between blotting-paper, and once recrystallizing, it is obtained quite pure. In this manner more æsculine is produced, at a less cost, in shorter time, and with less trouble than by any of the usual modes of preparation.

By dissolving the alumina precipitate in water containing acetic acid, filtering, precipitating the filtrate with a lead-salt, and decomposing this precipitate with sulphuretted hydrogen, the gallic acid is easily obtained.

It will be possible by this process to prepare many substances at a cheap rate which have hitherto found no application from their high prices.—*Journ. für Prakt. Chemie*, lxxi. p. 414.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Clarification of Sugars and Saccharine Matters by the employment of Soaps. By M. Basset.

This new method, discovered by Mr. F. Garcia, an old sugar manufacturer in Louisiana, obviates the inconveniences presented by the employment of hydrated lime for the clarification of the juices, at the same time retaining its real advantages. It is founded on the property possessed by lime of combining with fatty bodies either in a free state, or in the form of alkaline soaps. When saccharate of lime is brought in contact with a solution of soda soap, a remarkable decomposition takes place, in which the sugar is set free, the lime combines with the fatty acid of the soap, and the soda remains in the liquid, usually in a free state.

When clarification has been effected with an excess of lime and the scum has been removed, the liquid may be cooled below 104° F. and the solution of soap immediately made use of. It is poured gently into the syrup, which is stirred round; when the whole is well incorporated, the temperature is brought up to ebullition. At this point the temperature is suddenly lowered by stopping the access

of steam, and the new scum is removed; this is nothing but a lime soap, which has brought up all the impurities from the bottom to the surface. After the removal of this scum, the syrup is perfectly limpid and in taste is very pure.

This process has been tried on a large scale at the factory of Messrs. Bonzel, near Lille. The experiments were made each time upon 10 hectolitres of syrup, and second and third molasses, and were always successful. With very dilute syrups, the calcareous soap does not always rise completely; in these cases a simple passage through the filter-bag and filtration through animal charcoal are sufficient for complete clarification. The syrups are perfectly pure and free from odour; the odour of beet having completely disappeared. Crystallization is effected readily, the crystals are large and well formed and the sugar is dry.

The quantity of soap to be employed varies, and may be carried to the complete saturation of the lime. It appears, however, that half this quantity is sufficient, the beauty of the crystallization being greater when all the lime is not saturated. Syrups in a state of incipient fermentation must be saturated with alkali, as their carbonic acid destroys the saponaceous compound. No special apparatus is required.

The soap employed in the experiments was made with soda and olive-oil, but any soap may serve the same purpose. It must be more or less neutral according to the acid or alkaline qualities of the syrup to be treated, and the economy of its employment is increased by the fact, that the only expense is that of the soda for saponification and the acid for the decomposition of the calcareous soap, as the fatty matter serves almost indefinitely. The method also causes a considerable diminution in the employment of animal charcoal.—*Comptes Rendus*, December 28, 1857, p. 1097.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Dec. 10, 1857. (The Lord Wrottesley, President, in the Chair.)

"On the Chemical Action of Water on Soluble Salts." By Dr. J. H. Gladstone, F.R.S.

Before extending my researches on chemical affinity among substances in solution, it seemed desirable to ascertain, if possible, what specific chemical action water exerts on a salt. This inquiry is beset with unusual difficulties, and unfortunately my experiments have not led to any conclusive result. Yet some of the observations made during the course of the inquiry have a value independent of theory, and a brief notice of them may not perhaps be deemed unworthy of a place in the Proceedings of the Royal Society.

It is well known that many anhydrous salts will absorb water, and still remain solid bodies, either amorphous or crystallized. In such

a case the water combined is always in simple atomic relation with the salt itself; great heat is often evolved, and a change of colour frequently ensues. These "hydrated" salts (as they are usually considered) are generally soluble in water; and it is the condition of such a body when dissolved that opens a wide field for speculation. The water may act merely as a solvent; or it may unite without decomposition with the dissolved salt, becoming an integral part of the compound in solution; or reciprocal decomposition may ensue, each electro-positive element combining with each electro-negative one in certain proportions; or the ultimate result may be due to two or more of these modes of action in conjunction.

When a "hydrated" salt is dissolved in a minimum of water, nothing is usually observed beyond the new physical properties resulting from the change in its state of aggregation and the absorption of heat. No change of colour, as far as I can find, ever ensues, though a change in the amount of fluorescence may occur. When an anhydrous salt, which will not combine with water to form a solid compound, dissolves, a change of colour does sometimes ensue. Sometimes, however, an evident decomposition takes place, the hydrogen and oxygen of the water combining each with one of the elements of the other binary compound, and the products of this action remaining uncombined. Chloride of bismuth and citrate of ammonia are instances. But in the vast majority of instances, the salt MR and the water HO do not suffer reciprocal decomposition, unless indeed, as has been contended, the resulting MO, HR remain combined together in solution.

If a reciprocal decomposition of this character actually occurs, it may be anticipated by analogy, that by increasing the amount of HO, more MR will be decomposed. Now, if additional water be added to saturated aqueous solutions of pentachloride of antimony, ferric sulphate, ammoniacal nitrate of copper, or nitrate of bismuth, decomposition results, and a precipitate forms proportional within certain limits to the amount of water added; but not one of these is a salt of the simplest constitution. Sometimes, however, a change is rendered apparent in simple salts by a change of colour without the formation of a precipitate.

This was closely examined. It might be expected, *à priori*, that a certain amount of salt would have the same absorbent effect on a given quantity of light, whether it were dissolved in much or little water, and that as the absorbent power of water is practically *nil*, it would appear to the eye of precisely the same depth and character of colour in the two cases. And this actually holds good in the majority of instances; but to prove it a special contrivance was necessary, in order to make the same quantity of light impinge upon the solution before and after dilution. This was effected by means of colourless cylindrical glasses of uniform diameter and the same size, closed at one end with a flat plate of glass, so that when placed upright they could hold liquids: they stood in a case so contrived that all the light which passed through the strong or diluted solution, as looked through from above, had to enter by the flat plate

at the bottom. Every experiment was performed by a comparative method, two glasses being placed side by side, one containing the solution to be diluted, the other a similar quantity of the same solution which served as a standard.

In this manner it was determined that the following salts absorbed the same light whether dissolved in much or in little water :—

Ferrous Sulphate.
Ferric Nitrate.
Ferric Meconate.
Ferric Comenate.
Ferric Comenamate.
Ferric Gallate.
Nitrate of Nickel.
Nitrate of Cobalt.
Sulphate of Cobalt.
Chloride of Chromium.
Acetate of Chromium.
Chromate of Chromium.
Nitrate of Uranium.
Chloride of Uranium.
Sulphate of Ceric Oxide.
Terchloride of Gold.
Terbromide of Gold.
Protochloride of Platinum (in hydrochloric acid).
Bichloride of Platinum.
Bichloride of Palladium.
Chromate of Potash.
Ferrocyanide of Potassium.
Ferridcyanide of Potassium.
Nitroprusside of Sodium.
Sulphindigotic Acid.
Sulphindigotate of Ammonia.
Carbazotate of Copper.
Pentasulphide of Potassium.

The following salts were affected in regard to their absorption of light, by adding water to their saturated solutions :—

Salt.	Saturated solution.	Dilute solution.
Ferric Acetate.	Red.	Darker.
Ferric Tartrate.	Red.	Slightly paler.
Ferric Chloride.	Orange-red.	Orange-yellow.
Ferric Citrate.	Red.	Orange and paler.
Ferric Sulphocyanide.	Intense red.	Orange.
Chloride of Nickel.	Yellowish green.	Bluish-green.
Iodide of Nickel.	Deep green.	Paler blue-green.
Chloride of Cobalt.	Red.	Paler and less pure.
Iodide of Cobalt.	Deep green.	Pale red.
Acetate of Cobalt.	Red.	Paler and more orange.
Sulphocyanide of Cobalt.	Intense purple.	Pale red.
Chloride of Copper.	Green.	Blue.
Bromide of Copper.	Green.	Blue.
Acetate of Copper.	Greenish blue.	Paler and purer blue.
Permanganate of Potash.	Purple.	Paler and redder.
Chromic Acid.	Red.	Orange.

That these changes of colour are due to the action of the water, and not to any merely physical cause, is proved by the fact that alcohol does not occasion them. Quantitative experiments were instituted with acetate of copper and sulphocyanide of iron, to determine whether the effect of successive additions of water is in a decreasing ratio. It was found to be so on the whole, but the results showed certain irregularities that do not usually occur in cases of reciprocal decomposition, where the mass of one of the compounds is successively increased.

A prismatic examination of the rays absorbed by these salts in different states of solution revealed two very suggestive facts. The

one is, that in every case (except ferric acetate) the salt in dilute solution not only transmits every ray that was transmitted by it in saturated solution, but also some rays which it then absorbed. The other is, that strong solutions of the chlorides, bromides, and iodides of copper, cobalt, nickel, and iron—analogous metals—exhibit not only the absorption due to the respective bases, but another absorption which can be identified with that produced by the halogens themselves when simply dissolved in water; while, when these solutions are diluted, they cease to produce this second absorption, and give precisely the same prismatic image as any compound of the same base with a colourless acid. The amount of water required to effect this change depends on the temperature. That the phenomena indicate some difference of arrangement among the elements of the dissolved salt and the water, cannot, I think, be doubted, but they fail to show in any distinct manner what that difference is.

The action of water on double salts is a still more complicated problem; but the question as to whether water separates the two components did not prove so difficult of decision. While on the one hand the physical properties of many double salts, as for instance the potassio-chloride or iodide of platinum, prove that they are not decomposed by water, the experiments of Graham, on the other hand, show that some salts, as for instance alum, suffer at least a partial decomposition in diffusion.

The iodide of mercury and potassium, and the sulphocyanide of silver and potassium, dissolve in a small quantity of water, but the addition of more causes the separation of the insoluble component. The double sulphates of copper, nickel, or chromium with potash, the sulphate of copper and ammonia, the chloride of platinum and potassium, the iodides of platinum or gold with potassium, and the hydrochlorate of chloride of gold, do not change in colour on the dilution of their aqueous solutions; but this does not prove that no separation has taken place, for the colour of these double salts in solution is precisely that of an equivalent amount of that component to which the colour is due. But bichlorate of potash and bicomenamate of iron likewise exhibit no change of colour on dilution, though such must ensue, if they be converted into neutral salt and free acid. On the other hand, the red potassio-oxalate of chromium varies in intensity of colour on the addition of water, and the different double chlorides of copper undergo the same change as the simple salt. If hydrochlorate of terchloride of gold be added to the terbromide of that metal, a reduction in colour ensues, and an analogous result is obtained when the double sulphate of copper and potash acts on the acetate of copper—facts which point to a decomposition of the double salt in solution. Indeed it is evident that some double salts are resolved more or less into their components by water, while others are not so affected.

The general tendency of my observations has led me to the opinion, that water does not act upon a salt dissolved in it in a manner analogous to that of the hydracids, but I hesitate to draw any conclusion as to the rational constitution of a dissolved salt.

THE CHEMICAL GAZETTE.

No. CCCLXX.—March 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Oxidation of Albumen by Permanganate of Potash. *By* S. STÄDELER.

ALTHOUGH no one doubts that the urea which occurs in the urine of man and all the higher animals, is formed in the organs by processes of oxidation and decomposition from the proteine substances, all endeavours to prepare it therefrom by artificial means had produced no results, until at last Béchamp stated to the Academy of Paris that he had succeeded in that in which so many chemists had failed. The subject was of such great interest, and, as regarded the author, who had repeatedly occupied himself with the artificial formation of urea, so unexpected, that he immediately commissioned Neukomm to repeat Béchamp's experiments.

According to Béchamp, urea is produced from the albumen of eggs and of the blood, from blood-fibrine and from gelatine, when these are oxidized by permanganate of potash, sometimes with the careful addition of sulphuric acid, the temperature being kept as low as possible, so as never to exceed 176° F. For the most advisable dilution of the albumen (with which alone the more careful experiments appear to have been made), the proportion 1 : 30 is given; for the oxidation of 1 part of this nearly 7½ parts of permanganate of potash are required. From these data a repetition of the experiments presented no difficulty, especially taking into consideration Gregory's observation, that urea is not decomposed by permanganate of potash at a moderate temperature, with which Béchamp's statements also agree.

The experiments made in the laboratory at Zürich, have led to a result very different from that of Béchamp; even the quantity of permanganate of potash required for the oxidation of the albumen is scarcely half so much as that stated by him.

50 grms. of white of egg (consequently about 6 grms. of albumen) were diluted to 180 grms., poured through a cloth, mixed with 18 grms. of permanganate of potash, and heated continuously to 122°—131° F. The action took place very slowly, although from

time to time dilute sulphuric acid was dropped in, so that the alkaline reaction of the fluid was always weak. When decolorization had taken place, a sample of the slightly alkaline fluid was no longer rendered turbid by heat, or on the addition of a drop of acetic acid. An additional 4 grms. of permanganate of potash were then put in, and the fluid was heated for several hours to the same temperature as before. The red colour of the fluid disappeared, but not completely, so that the oxidation was to be regarded as completed (for this temperature; although not more than about $3\frac{1}{3}$ parts of permanganate of potash had been employed to 1 part of albumen).

To decompose the permanganate of potash still present, a few drops of alcohol were added, and the decolorized solution was filtered. The reaction gradually became alkaline again, and therefore a drop of sulphuric acid had to be added from time to time. We know from long experience, that under these circumstances no urea is destroyed by the heat of the water-bath.

The residue of evaporation was treated with hot absolute alcohol, and after standing for 24 hours, the solution was poured away from the deposit, which consisted of sulphate of potash and a yellowish syrup, and evaporated to a small volume. In the residue no crystals of urea made their appearance, but when nitric acid was added, an abundant crystalline deposit was produced, with evolution of acetic and formic acids; this certainly had some resemblance to nitrate of urea, but could not be taken for that salt without further investigation. After standing for 24 hours, the crystalline paste was put upon bibulous paper, the crystals freed from the mother-liquor were repeatedly pressed between fresh layers of paper, and visible intermixed crystals of nitrate of potash carefully picked out.

If the crystallization consisted of nitrate of urea, pure urea must have been obtained from it with ease. Water was therefore poured over it, and it was digested with carbonate of baryta until the acid reaction had disappeared; it was then filtered and evaporated, and the residue extracted with absolute alcohol.

By the evaporation of the solution an indistinctly crystalline mass was obtained, which was repeatedly treated with alcohol in order to extract urea. In each treatment a difficultly soluble residue remained, but during the spontaneous evaporation of the alcoholic solutions, no crystal was ever obtained bearing even the most distant resemblance to urea.

The residue of evaporation had at last become very small; it had the aspect of a sandy powder, in which small, isolated colourless laminæ and warts, consisting of delicate entangled needles, were detected under the microscope. The author observed that the colourless laminæ dissolved very readily in alcohol, but the warts with difficulty, so that the hot saturated solution deposited a portion of them again even whilst cooling; on the other hand, they were readily taken up by water. The solution contained baryta and dilute acids, even acetic acid produced a crystalline deposit in it. When the baryta-compound was heated in a glass tube, it fused and

became black, and white vapours with scarcely any action upon red litmus-paper were evolved, which condensed into oleaginous drops with an odour like that of benzole. The author then dissolved the entire remaining residue in a small quantity of boiling water, added muriatic acid to it, and allowed it to cool slowly, when a crystallization was produced consisting of delicate, colourless laminæ, mostly grouped in a stellate form. The crystals were extremely difficult of solution in cold water, but dissolved with ease in boiling water; they were also soluble in alcohol and æther. The solutions had an acid reaction. In a glass tube the crystals fused into colourless drops, which solidified in a crystalline form on cooling. Even with a strong heat no carbonization occurred; the melted drops crept up the sides of the tube, and the fumes evolved, which were provocative of coughing, condensed in a crystalline form in the upper part of the glass tube. When the crystals were heated with soda-lime, no ammonia was evolved, and the same odour like benzole was again produced, as before when the baryta-compound was heated.

Small as the scale was on which these experiments were made, all the reactions agree so completely with those of benzoic acid, that there can be no doubt as to its formation during the oxidation of albumen by permanganate of potash, and the less, as Guckelberger has already discovered this acid amongst the products of the oxidation of the proteine substances by chromic acid, and also by oxide of manganese and sulphuric acid. It is worthy of notice, however, that by the action of permanganate of potash a comparatively very considerable quantity of benzoic acid is produced; for by the employment of only 6 grms. of albumen, the precipitate first produced by nitric acid, of which a great deal was lost during the subsequent attempts at purification (by the repeated solution of the benzoate of baryta in alcohol), was so great, that it would certainly have sufficed for an elementary analysis. This also throws some light upon the formation of hippuric acid in the organism; no doubt the benzoic acid which we assume to be a conjunct therein, is formed in the body from the proteine substances, and there exists no foundation for the assumption that it only reaches the body of the Herbivora by means of their food-plants.

Béchamp does not say anything of the occurrence of benzoic acid amongst the products of oxidation of albumen, and we must therefore suppose that he took it for nitrate of urea. That after the complete oxidation of albumen, the substance (benzoate of potash) extracted by alcohol from the residues of evaporation gave a precipitate not only with nitric acid, but also with oxalic acid and nitrate of mercury, agrees perfectly with this view, and the author therefore regards it as a mere embellishment of his work with analytical results, that Béchamp adds, that the mercurial compound has the composition $4HgO, C^2 H^4 N^2 O^2$, and that by the action of nitrate of mercury containing nitrous acid, a mixture of nitrogen and carbonic acid was obtained, in the volume-proportion of 2 : 1, and consequently such as is met with in the decomposition of urea.—*Journal für Prakt. Chemie*, lxxii. p. 251.

On Cupreous Oxide of Manganese from Chile.

By Frederick Field, M.R.I.A., F.C.S.*

Coquimbo, January 16, 1858.

A mineral containing the oxides of manganese and copper has been obtained from the tin mines of Schlackenwald in Bohemia, and examined by Kersten. The following is the result of his analysis:—

Peroxide of manganese ..	74·10
Oxide of copper	4·80
Peroxide of iron	·12
Sulphate of lime	1·05
Silica	·30
Water	20·10
	100·47

It is described in various mineralogical works as a very rare substance. In Chile large quantities of a mineral consisting essentially of the oxides of copper and manganese in combination with silica and water, are obtained, and termed by the miners of that country *Metal de carbon*, from its great similarity in appearance to ordinary coal, having a bright shiny aspect, and being perfectly black. It is generally found associated with the blue and green silicates of copper, although occasionally with the native metal and its red oxide.

The following is an analysis of a specimen taken from a large lump of the mineral from a mine in the province of Coquimbo in which it abounds.

100 grs. yielded—

Peroxide of manganese ..	40·28
Oxide of copper	24·71
Silica	18·90
Oxide of iron	·23
Water	15·52
	99·64

When heated, it loses water and oxygen, the peroxide of manganese becoming converted into manganoso-manganic oxide. It dissolves in hydrochloric acid, even in the cold with copious elimination of chlorine, the silica separating as a fine white powder, never assuming the gelatinous modification. 100 grs. heated in a platinum crucible to bright redness, until no diminution of weight took place, lost 19·85 grs., showing that the whole of the manganese exists as peroxide.

100 grs. of mineral contain 15·52 water and 40·28 peroxide of manganese, which on ignition should lose 4·81 oxygen, and yield 35·47 $Mn^3 O^4$.

Oxygen....	4·81		100·00
Water	15·52		19·85
100·00 —	20·33=79·67	Found..	80·15

* Communicated by the Author.

Immense quantities of cupreous manganese exist in a mine near Jambillos in the same province, associated with red oxide of iron, carbonate of lime, and silica.

The following is a rough analysis of a sample taken from about 200 tons of the mineral, and will serve as an illustration of the produce of the mine in question:—

Peroxide of manganese.....	18·2
Oxide of copper	6·5
Oxides of iron	24·6
Carbonate of lime.....	28·0
Water	4·8
Residue consisting of silica, &c.	16·6
	98·7

It is used extensively in the various copper-smelting establishments in Coquimbo, as a flux for the hard siliceous ores. I have met with the same mineral in the north of Chile, on the confines of Bolivia, and in Peru.

On Pimelic Acid and some of its Compounds. By E. MARSH.

When oleic acid is treated with nitric acid, there are produced, as we know from the first investigations of Laurent, and the subsequent ones of Bromeis and Redtenbacher, suberic acid, pimelic acid, adipic acid, lipic acid, azelaïc acid, and azoleic acid, besides acids belonging to the series $C^n H^n O^4$. The author has worked upon the separation of pimelic acid from the accompanying acids, and also upon some of its compounds.

The pimelic acid is prepared as follows:—Oleic acid is treated with nitric acid. The sebacic acid is first of all allowed to crystallize from the solution. The fluid thus separated is concentrated, the mixture of acids obtained is pressed between paper, then dissolved in water, and carbonate of soda is added to the hot solution until a slight alkaline reaction is produced. Suberate of baryta is thrown down by solution of chloride of barium, sulphate of copper is added to the fluid separated from this precipitate, the pale blue precipitate of pimelate of copper is washed, diffused in water, and decomposed by sulphuretted hydrogen. The fluid is then concentrated; the first crystals which separate are removed, as they probably still contain suberic acid, and those which subsequently make their appearance are collected as pimelic acid.

Pimelic Acid, $C^{14} H^{12} O^8$, prepared in this way, crystallizes from its aqueous solution, in hard, wart-like crystals, aggregated in a stellate form. It has a somewhat acid taste; the perfectly dry acid becomes soft at 233° F., and fuses at 237°—239° F. It dissolves pretty readily in cold water, abundantly in hot water, and without difficulty in alcohol and æther.

Salts of Pimelic Acid.—The solutions of neutral salts of the heavy metals, precipitate the solution of pimelate of ammonia. The *copper-salt* contained 35·2 and 34·25 of oxide of copper (calculated

35·86 per cent.), corresponding with the formula $C^{14} H^{10} O^6 + 2CuO$. The *silver-salt*, dried at 212° F., gave 61·15 per cent. of oxide of silver; the formula $C^{14} H^{10} O^6 + 2AgO$, requires 62·03 per cent.

Pimelate of Oxide of Amyle, $C^{14} H^{10} O^6 + 2C^{10} H^{11} O$, is obtained by passing muriatic acid gas into the solution of pimelic acid in amylic alcohol. The fraction passing at 266° F. is distilled off, muriatic acid gas is again passed into the residue mixed with a fresh quantity of alcohol, and all that passes at 266° F. is distilled off.

The dark red residue only boils at 500° F., and but for a short time at this temperature; the thermometer rose to 536° F., whilst a dark red oily fluid passed over. This fluid is rectified with that extracted by alcohol from the blackened residue in the retort; the fraction passing below 302° F. is separated, and that passing at 338°—392° F. is collected.

This distillate is an oleaginous fluid, of a penetrating and not agreeable odour, insoluble in water. It is soluble in alcohol and æther. Analysis gave numbers corresponding with pimelate of oxide of amyle:—

C	67·82	67·47
H	10·88	10·92
O	..	..

Pimelate of Oxide of Æthyle, $C^{14} H^{10} O^6 + C^4 H^5 O$, prepared in the same way as the preceding body, removing the fraction passing below 212° F. during rectification. It is a fluid with a pleasant fruit-like odour. It boils temporarily at 365° F., but the thermometer soon rises, and carbon separates. The portion now distilled appears to be the acid æther, $C^{14} H^{10} O^6 + HO, C^4 H^5 O$.

Pimelate of Oxide of Methyle is obtained in a similar way; it decomposes when boiled.—Liebig's *Annalen*, ciii. p. 121.

On Scammony. By Dr. Franz Keller.

The author first of all purified commercial scammony, by dissolving it in alcohol and adding animal charcoal to it whilst boiling. This solution was mixed with water until it became turbid, and again treated once or twice with animal charcoal until it became colourless.

The alcohol was then distilled off, the residue mixed with water, and evaporated. By this means the resin separates in a soft state, and when drawn out into threads acquires the most beautiful silky lustre. The resin was boiled several times with water, by which it became brittle. It may be easily pounded into a perfectly white powder. The analysis gave—

C	56·69	56·67	76	= 456	56·78
H	8·34	8·42	67	67	8·34
O	..	..	35	280	34·88

Scammonic Acid, $C^{76} H^{64} O^{43} + 4HO$.—If the resin be put into a boiling solution of baryta, it is dissolved with evolution of an aromatic odour, resembling that of oil of hops, and forms a clear fluid.

From this solution muriatic acid does not precipitate the resin. The baryta is thrown down by sulphuric acid in slight excess, and carbonate of lead is then added to get rid of the excess of sulphuric acid; lastly, a small quantity of lead is thrown down by sulphuretted hydrogen. In this way a strongly acid fluid is obtained, which, when evaporated, leaves an amorphous, cracked, gum-like mass, exhibiting no trace of crystallization. This mass is allowed to stand for a long time, by which means stellate groups of a fatty body, insoluble in water, separate; these are easily removed by dissolving the residue in water.

The author has analysed the lead-salt of this acid. It was obtained by slightly supersaturating the solution of the acid with ammonia, and then adding solution of acetate of lead. The analysis gave—

C	34·55	76 = 456		34·77
H	5·23	64	64	4·88
O	26·86	43	344	26·29
PbO	33·36	4	446·4	34·06

If the solution of this acid, or that of the resin in solution of potash be boiled with an excess of sulphuric acid, oil-drops gradually separate on the surface; these solidify in a crystalline form. They are purified by repeated washings. This substance is the author's

Scammonolic Acid, $C^{36}H^{36}O^{7}$.—An acid fusible at 131—133°, insoluble in water, soluble in alcohol and æther. Its solutions have a strong acid reaction. From alcohol the acid crystallizes in microscopic needles. The analyses gave—

C	70·01	69·74	70·28	36 = 216		70·13
H	11·95	12·03	12·06	36	36	11·68
O	..	..	..	7	56	18·19

The sulphuric acid fluid from which this acid separates, contains sugar in abundance. According to a quantitative determination, the resin contains 46·2 per cent. of sugar.

The volatile body which distils over when scammonic acid is boiled with sulphuric acid, is butyric acid.

From these results the author concludes, that the so-called scammony resin contains a hydrate of carbon, $C^{12}H^{10}O^{10}$ (dextrine?), conjugated with several acids. It is a glucoside of the formula

$$C^{76}H^{67}O^{35} = C^{76}H^{64}O^{32} + 3HO.$$

When boiled with caustic alkalies, there is produced from the glucoside an acid, scammonic acid, which, with an equal number of equivalents of carbon, is distinguished from the anhydrous resin by an addition of 4 equivs. of hydrogen and 11 of oxygen, and consequently by 4 of water and 7 of oxygen. Four of these equivs. of water are replaceable by metallic oxides. By the action of dilute mineral acids upon the glucoside acid, or the alkaline solution of the resin, the acid splits up into a new acid, scammonolic acid,

$$C^{36}H^{36}O^{7},$$

and sugar. A volatile acid is also formed, which was recognized as butyric acid.

The products of decomposition obtained, when put together, give—

$C^{36} H^{36} O^{7}$ 1 equiv. scammonolic acid,
$C^{24} H^{24} O^{24}$ 2 equivs. sugar,

an atomic complex of.. $C^{60} H^{60} O^{31}$

If this be deducted from hydrated scammonic acid,

$C^{76} H^{68} O^{47}$
$C^{60} H^{60} O^{31}$

there remains.. $C^{16} H^{8} O^{16}$, of which
$C^{8} H^{8} O^{4}$ 1 equiv. butyric acid,

$C^{8} O^{12} = 4(C^{2} O^{3})$ oxalic acid.

The splitting process is therefore as follows:—

$$C^{76} H^{64} O^{32} + 4HO + 11O = 2(C^{12} H^{12} O^{12}) + C^{8} H^{8} O^{4} + 4(C^{2} O^{3}) + C^{36} H^{36} O^{7}.$$

The presence of the oxalic acid which occurs in these equations was not ascertained by the author.—Liebig's *Annalen*, civ. p. 63.

On Franguline. *By* Dr. Arthur Casselmann.

Buchner discovered a yellow colouring matter in the bark of *Rhamnus frangula*, and called it rhamnoxanthine. In the state in which Buchner obtained this body, it was not a pure substance according to the author's experiments. The author therefore names the pure colouring matter

Franguline; it is prepared as follows:—The powdered bark is first extracted at a boiling heat with water containing ammonia. The dark red filtrates are mixed with muriatic acid, and left to settle quietly. With the first extract this usually takes several weeks; with the following one only a few days. The blackish-brown precipitates are separated by filtration, washed, and treated with boiling alcohol of spec. grav. 0·863, with the addition of neutral acetate of lead. Nearly the whole precipitate dissolves in alcohol with an intense brown colour. Impurities, such as tannine, &c., are thrown down by acetate of lead, whilst the solution, which is heated whilst still hot, contains the colouring matter in solution. This solution is now mixed with water until a strong turbidity is produced, heated until the latter again disappears, and left to stand quietly. After several weeks the franguline is deposited already in a somewhat crystalline form; it is recrystallized from boiling alcohol until it separates with a silky lustre from the solution whilst still hot. It is only in this way that the obstinately adherent, amorphous, resinous colouring matter can be removed, but at the same time a great loss of material can hardly be avoided.

Franguline is obtained more rapidly when the alcoholic solution, after being filtered from the precipitate of acetate of lead, is agitated with hydrated oxide of lead, or in the absence of this, with basic

acetate of lead, by which all the franguline is precipitated. The washed precipitate is treated with very dilute alcohol, and decomposed by the passage of a strong current of sulphuretted hydrogen gas. The sulphuret of lead formed retains the greater part of the resinous colouring matter, when this paste is extracted with boiling alcohol. The solution thus obtained is diluted with a small quantity of water, and the franguline which is deposited purified by repeated recrystallization from alcohol.

Properties.—Pure franguline forms citron-yellow crystalline masses with a dull silky lustre. Under the microscope transparent quadratic prisms are recognized. It fuses at about 480° F., and at the same time sublimes in golden-yellow, microscopic needles. It is inodorous, tasteless, and nearly insoluble in water, but perfectly soluble in 160 parts of hot alcohol of spec. grav. 0·863. Cold æther dissolves scarcely any of it, but it dissolves in fatty oils, benzole and oil of turpentine. Concentrated sulphuric acid dissolves it even in the cold with a dark ruby-red colour, which passes into brown on the application of heat; on the addition of water it again becomes yellow. In boiling concentrated nitric acid it dissolves completely, but separates unchanged on cooling in golden-yellow microscopic needles. By fuming nitric acid it is but little altered in the cold, but on the application of heat is changed in such a way, that, besides oxalic acid, a nitrocompound, crystallizing in golden-yellow microscopic needles, to which the author has given the name of *Nitrofrangulic acid*, is formed. Alkalies dissolve franguline with a splendid purple-red colour; ammonia only dissolves it after some time in the cold, but immediately when heated. From these solutions it is again thrown down with a yellow colour by acids. Metallic salts do not precipitate it, but most of the hydrated metallic oxides form lakes with it, some of which are of beautiful colours. Notwithstanding all his care the author found it impossible to obtain a definite chemical compound with bases. Analyses:—

C	57·35	57·01	57·22	12=72	57·1
H	4·92	4·99	5·04	6 6	4·7
O	37·73	38·00	37·74	6 48	38·0

Franguline, $C^{12} H^6 O^6$, has much similarity with chrysophanic acid, but still exhibits a sufficient difference from that acid.

Nitrofrangulic Acid, $C^{40} H^{10} O^{16}, 5NO^4 + HO$, is produced by the careful treatment of franguline with fuming nitric acid. When crystallized from water, it forms small yellow crystals; from alcohol it crystallizes in long, silky, orange-coloured needles, grouped in a stellate form. Its taste is rather bitter and astringent; it colours the saliva purple-red, and has no odour. When heated it puffs up, leaving a coal which is difficult of combustion. It is but slightly soluble in cold water, but dissolves completely in boiling water with a dark crimson colour; from this solution it separates again slowly on cooling in crystalline flakes, and more rapidly on the addition of acids. The smallest quantity of alcohol or æther immediately produces a dark red solution. On the evaporation of the solution

the acid is left of a yellow colour. Concentrated acids scarcely act upon it in the cold. By concentrated sulphuric acid it is rendered pale yellow, and becomes reddish-brown on being heated. Concentrated nitric acid dissolves it, and it crystallizes from this solution again in golden-yellow, microscopic needles. Alkalies dissolve it with a violet-red colour. Salts of baryta, strontia, and lime furnish precipitates of a fiery-red colour with a solution of nitrofrangulic acid; salts of lead and cadmium behave in the same way: the most remarkable compounds are those of copper and silver. If sulphuretted hydrogen gas be passed continuously through a hot solution of the acid in water, the dark red solution very soon passes into violet blue with deposition of sulphur; the colour thus produced is heightened by the addition of alkali. On the addition of muriatic acid a violet blue precipitate is produced. Analysis gave,—

C	39·0	40	=240	38·8
H	1·9	11	11	1·7
N	11·4	5	70	11·3
O	47·7	37	296	47·9

Its formation from franguline is

$$4(C^{19}H^{6}O^{6})+14(NO^{4}\text{ dissolved in }NO^{5})=$$
$$C^{40}H^{10}O^{16}\,5NO^{4}+HO+4(C^{2}O^{3}+HO)+9HO+9NO^{2}.$$

The hot solution of nitrofrangulic acid in water, as well as in alcohol, furnishes, on the addition of nitrate of silver,

Nitrofrangulate of Silver, $C^{40}H^{10}O^{16}, 5NO^{4}+AgO$, in cinnabar-red, prismatic needles with a dull silky lustre. It is readily soluble in alcohol and æther, with a dark ruby-red colour, sparingly in cold, but completely in hot water. When heated by itself it explodes with a violent detonation, for which reason in the analysis the determination of the amount of oxide of silver could not be effected by mere ignition in a porcelain capsule. Analysis gave,—

C	33·0	40	=240	33·1
H	1·5	10	10	1·3
N	9·6	5	70	9·6
O	39·9	36	288	39·7
AgO	16·0	1	116	16·0

Nitrofrangulate of Copper, $C^{40}H^{10}O^{16}, 5NO^{4}+CuO$, separates as a violet-blue, silky substance, when the alcoholic solution of the acid is added to that of acetate of copper. It is very sparingly soluble in cold water, rather more so in alcohol and æther, and dissolves readily in acetic acid with a violet-blue colour. On the addition of concentrated muriatic acid, the solution becomes red by the liberation of nitrofrangulic acid. When heated it explodes with a far stronger detonation than the silver salt. Analysis of the salt dried at 212° F.:—

C	37·1	40	=240	37·0
H	1·8	10	10	1·5
N	10·8	5	70	10·8
O	43·7	36	288	44·4
CuO	6·6	1	39·7	6·1

The composition of franguline stands in close connexion with that of the colouring matter of the root of madder. We have—

Franguline	$C^{12} H^6 O^6$
Alizarine	$C^{20} H^6 O^6 + 4HO$
Purpurine	$C^{18} H^6 O^6 + HO$.

Liebig's *Annalen*, civ. p. 77.

On Sulphosalicylic Acid and Conjugate Acids. *By* O. Mendius.

The author prepares salicylate of potash from oil of Gaultheria by the method of Cahours with concentrated solution of potash. This salt he decomposes by means of muriatic acid, collects the separated acid upon a filter, and recrystallizes it from its solution in hot water. The perfectly dry acid is exposed to the vapour of anhydrous sulphuric acid, by which means sulphosalicylic acid is obtained. This is saturated with carbonate of baryta. From the solution separated from the sulphate and carbonate of baryta, the sulphosalicylate of baryta separates; the mother-liquors furnish a further quantity of it when evaporated. The author obtained the crystals in three different forms, but their composition was the same; the difference is therefore probably caused only by the different concentration of the solutions from which the crystals were deposited, by the greater or less purity of the salt, &c. The following are analyses of the baryta-salt obtained in small, transparent, hard crystals (A), in light, delicate, silky needles (B), and in small, roundish warts (C):—

	Found.						
	A.		B.		C.		Calculated.
6HO	11·5	12·92	11·72	13·14	11·7	13·1	13·26
2Ba	33·8	33·8	33·4	33·8	33·57	33·65	33·66

These baryta-salts therefore have the formula $C^{14} H^4 Ba^2 S^2 O^{12} + 6HO$.

The author now tried whether any still more basic salts could be prepared, that is to say, as the preceding analyses led to the formula $\left.\begin{matrix} C^{14} H^4 S^2 O^8 \\ Ba^2 \end{matrix}\right\} O^4$, whether this formula itself was not $\left.\begin{matrix} C^{14} H^3 S^2 O^6 \\ H^1 Ba^2 \end{matrix}\right\} O^6$.

He mixed a hot solution of caustic baryta with a hot solution of the preceding baryta-salt; no new baryta-salt with a larger amount of baryta was produced, but the preceding salt was again furnished.

Sulphosalicylate of Baryta, $C^{14} H^4 Ba^2 S^2 O^{12} + 6HO$, is readily soluble in hot, less so in cold water, and perfectly insoluble in æther or alcohol. If it be strongly heated, phenylic alcohol is evolved. From the baryta-salt the free acid is obtained, either by precipitating the baryta with exactly the proper quantity of sulphuric acid, or by adding sulphuric acid in slight excess, and saturating this solution

with carbonate of lead. In this way the lead-salt is obtained, and this is afterwards decomposed by sulphuretted hydrogen.

Sulphosalicylic Acid crystallizes from the very concentrated solution in irregular six-sided prisms; it is soluble in water, alcohol and æther in all proportions, and deliquesces in the air. It is a very stable, strong acid, the solution of which dissolves zinc with evolution of hydrogen; it is not decomposed when heated either with dilute or concentrated sulphuric or nitric acid. When boiled with a mixture of both, however, the fluid becomes turbid and reddened, and on its cooling light crystalline flakes of a yellow body separate. In this operation sulphosalicylic acid is decomposed into its constituents, sulphuric and salicylic acids, and the latter for its part undergoes the well-known further change into perchloride of chinone or chloranile; the yellow body, when heated, was found to be this, by its characteristic odour and the appearance of its sublimate. When heated by itself, sulphosalicylic acid fuses without decomposition at about 248° F., and solidifies on cooling in a radiate mass; at a higher temperature decomposition commences with the appearance of a brown colour, salicylic acid is sublimed in beautiful crystals, and phenylic alcohol makes its appearance.

The salts of this acid were obtained either by mutual decomposition, or by saturating the free acid with bases or their carbonates.

Sulphosalicylate of Soda, $\left.\begin{matrix} C^{14} H^4 S^2 O^{12} \\ Na^2 \end{matrix}\right\} + 6HO$, forms small, irregular six-sided prisms, readily soluble in water, insoluble in æther or alcohol. It only loses all its water of crystallization at 392° F. Analysis:—

C	32·13	14	32·13
H	1·93	4	1·53
Na	17·59	2	17·59
S	12·6	2	12·6

Sulphosalicylate of Potash, $C^{14} H^4 K^2 S^2 O^{12} + 4Aq$, is very soluble in water, and very slightly so in alcohol or æther.

The *Silver-salt*, $C^{14} H^4 Ag^2 S^2 O^{12} + 2Aq$, is difficult of solution in cold water, and dissolves readily in hot water, but not in alcohol. A hot concentrated aqueous solution sets, on cooling, into a stiff jelly, which only disappears after the lapse of a considerable time, as the salt settles to the bottom in the form of a heavy coarse powder. This consists entirely of perfectly round, small globules, which exhibit crystallization when crushed under the microscope. If the solution be boiled for a long time, some metallic silver separates. When heated, the salt begins to fuse and then becomes strongly inflated and decomposed.

The *Lead-salt*, $C^{14} H^4 Pb^2 S^2 O^{12}$, only crystallizes indistinctly in small round warts. It is but sparingly soluble in cold water, and insoluble in alcohol, which even separates it in flakes from dilute solutions. When heated, it fuses and becomes inflated, when ignited, it smoulders away.

The *Copper-salt* was obtained by the author in the form of a

heavy powder of a bright green colour, above which the rest remained as a tenacious varnish. When this mass was treated with alcohol nothing was dissolved; water left the green powder, whilst the solution, as before, resisted every attempt to bring it to crystallize. It reacted strongly acid, from which circumstance it is probable that the compound had been split into an acid and a basic salt. The amount of copper in the green powder, which, when examined under the microscope, was found to consist of small stellate needles, was determined in the humid way; the analysis led to the formula of a basic salt, $C^{14} H^4 Cu^2 S^2 O^{12} + 4HO$.

The *Copper-salt*, $C^{14} H^4 Cu^2 S^2 O^{12}$, in green cauliflower-like forms, which exhibit crystallization under the microscope, is obtained by the decomposition of the baryta-salt with sulphate of copper, when the strongly concentrated solution is allowed to cool over sulphuric acid. It is extremely soluble in water, stable in the air, and difficult of solution in alcohol.

The *Lime-salt*, $C^{14} H^4 Ca^2 S^2 O^{12} + 2HO$, forms very small, light, silky needles, united into hemispheres, which are soluble in water and insoluble in alcohol and æther.

The *Magnesia-salt*, $C^{14} H^4 Mg^2 S^2 O^{12} + 6HO$, crystallizes in tolerably long rectangular prisms of but little lustre, crossing each other irregularly, which lose their transparency by exposure to the air.

The *Zinc-salt*, $C^{14} H^4 Zn^2 S^2 O^{12} + 6HO$, agrees exactly with the magnesia-salt in its crystalline form, its degree of solubility, and its behaviour in the air. It may be ignited, and burns away with a clear light.

The acid sulphosalicylates are easily obtained by dividing the solution of the neutral baryta-salt into two equal parts, precipitating the baryta from one of them by sulphuric acid, and adding this acid solution to the other part; or by saturating one of two equal portions of acid with base, and then mixing the two portions and evaporating. In this way the author obtained—

The *Acid Baryta-salt*, $C^{14} H^5 BaS^2 O^{12} + 4HO$.—It crystallizes in oblique, irregularly six-sided, perfectly transparent prisms, of a strong glassy lustre. They are readily soluble in water, insoluble in alcohol and æther, and stable in the air.

The *Acid Soda-salt*, $C^{14} H^5 NaS^2 O^{12} + 4HO$, forms very light, thin, rhombic laminæ of a silky lustre, which dissolve readily in water, but with difficulty in alcohol. Undergoes no change in the air.

The *Acid Potash-salt*, $C^{14} H^5 KS^2 O^{12} + 4HO$, is produced from the hot concentrated solution in tolerably large globular groups, composed entirely of very fine needles. The crystals, when collected, form a very light mass of a strong silky lustre. In the moist state, they quickly redden in the air; they dissolve readily in water, but are insoluble in alcohol.

Another *Acid Potash-salt*, of the formula $C^{14} H^4 K^2 S^2 O^{12}$, $C^{14} H^5 KS^2 O^{12} + 2HO$, was obtained by the author from a mixture of the neutral salt with less free acid than the salt contained. This salt crystallizes in very thin, light, strongly silky needles; it is readily soluble in water, but insoluble in alcohol.

Sulphosalicylate of Potash and Soda, of the formula $C^7 H^4 KNa S^2 O^{12} + 8HO$, was obtained by neutralizing the acid potash-salt with carbonate of soda. On the cooling of the very concentrated hot solution it crystallizes in small, very silky, rectangular prisms. It is insoluble in alcohol and æther. The analysis made by the indirect method gave 11·19 K and 6·57 Na.

The sulphosalicylates, like the free acid, give an intensely violet colour to solutions of peroxide of iron, although the tint is more reddish than that produced by salicylic acid. They only lose their water of crystallization completely at 356° to 392° F., and most of them are not decomposed except at a considerably elevated temperature. When submitted to dry distillation, the neutral salts evolve phenylic alcohol; the acid salts furnish, besides this, a sublimate of salicylic acid.

Under no conditions could a salt containing more than 2 atoms of base be prepared; and in connexion with this it must be expressly observed that the author purposely arranged the conditions in such a way that the acid must have taken up 3 atoms of base, if it was its nature to saturate 3 equivs. of base.

Æther, $C^{14} H^4 (C^4 H^5)^2 S^2 O^{12}$, as a neutral, non-acid body. For its preparation, perfectly dry sulphosalicylate of silver, $C^{14} H^4 Ag^2 S^2 O^{12}$, was enclosed in a glass-tube with the calculated quantity of iodide of æthyle. When the action commences instantly at the ordinary temperature, the preparation may even be effected in open flasks. The product is extracted with æther, which is afterwards evaporated with the excess of iodide of æthyle; the sulphosalicylic æther is obtained in small, dazzling white, silky crystals, which under the microscope exhibit a great resemblance to the ordinary crystals of sulphate of lime. They are soft to the touch, and become tough and ductile like wax, even between the fingers; at 133° F., they fuse without decomposition, and the mass remains doughy and soft far below this temperature. This æther is formed in accordance with the equation

$$C^{14} H^4 Ag^2 S^2 O^{12} + 2C^4 H^5, I = 2AgI + C^{14} H^4 (C^4 H^5)^2 S^2 O^{12};$$

so that, as regards the formation of this æther, sulphosalicylic acid is bibasic. A disulpho-acid could not be prepared.

These are the essential facts contained in the author's memoir. It appears therefrom that sulphosalicylic acid is not tribasic. Throughout it appears to be bibasic.

At the same time it must be particularly remarked that the author himself performed this investigation for the discovery of the nature of salicylic acid, and that it stands in connexion with Limpricht's investigations of salicylic acid; it was performed in Limpricht's laboratory.

The question to be answered was whether salicylic acid is monobasic or bibasic; and the answer to this qustion was to be obtained by testing the conjugate sulpho-acid. As the sulpho-acid of salicylic acid is bibasic, salicylic acid should be monobasic, in accordance with the law propounded by Gerhardt as to the basicity of

conjugate compounds. The compounds prepared by Limpricht some time since, on the contrary, are in favour of its being bibasic.

The author considers it not improbable that all the facts taken together prove that the grouping of the atoms in salicylic acid may change, so as to produce at one time a monobasic and at another a bibasic acid radical, and consequently a monobasic salicylic acid of the formula $\left.\begin{matrix} C^{14} H^5 O^4 \\ H \end{matrix}\right\} O^2$, and a bibasic one of the formula $\left.\begin{matrix} C^{14} H^4 O^2 \\ H^2 \end{matrix}\right\} O^4$.—Liebig's *Annalen*, ciii. p. 39.

On the Preparation of Œnanthylene from Œnanthole. *By* H. Limpricht.

The results of C. Wicke's investigation of chlorobenzole have led the author to test the behaviour of the aldehydes of the fatty acid series towards perchloride of phosphorus. Hitherto only one aldehyde has been investigated in this direction. Chancel obtained from *butyral* the compound

$$\left.\begin{matrix} C^8 H^7 \\ Cl \end{matrix}\right\}.$$

The author allows 1 equiv. of œnanthole to flow gradually upon 1 equiv. of perchloride of phosphorus. A strong reciprocal reaction takes place; oxychloride of phosphorus distils over. After the completion of the reaction, the distillate boiling below 302° F. is separated from that which passes at a higher temperature. The latter is washed with water; the oil floating upon the water is agitated with a solution of bisulphite of soda, dried over chloride of calcium, and rectified. The distillate passing between 356° and 392° F. is nearly pure protochloride of œnanthylene. It is rectified again, and only the portion passing at 368°·6 F. is collected.

Protochloride of Œnanthylene, $C^{14} H^{14} Cl^2$, is limpid and very fluid; its odour is not unpleasant, similar to that of œnanthole; it is lighter than water, and boils at 375°·8 F.

Sodium, when assisted by a gentle heat, acts violently upon protochloride of œnanthylene, producing chloride of sodium and œnanthylene.

Chlorœnanthylene, $\left.\begin{matrix} C^{14} H^{13} \\ Cl \end{matrix}\right\}$.—If the preceding compound be boiled with an alcoholic solution of potash (15 grms. of protochloride of œnanthylene must be boiled for at least 8 days with a very concentrated solution of potash), this chloride is obtained. The same object is obtained more rapidly, but not more conveniently, by heating the protochloride of œnanthylene with alcoholate of potassium to 482° F. in sealed tubes; in this case the author expected the formation of a double æther,—

$$C^{14} H^{14} Cl^2 + 2C^4 H^5 KO^2 = \underset{\text{Æthylœnantholic æther.}}{\left.\begin{matrix} C^{14} H^{14} \\ (C^4 H^5)^2 \end{matrix}\right\} O^4} + 2KCl,$$

but obtained exactly the same product as by the employment of

alcoholic solution of potash. By diluting the mixtures with water, after they have been heated long enough, impure chlorœnanthylene is separated; this is dried with chloride of calcium, and distilled with an immersed thermometer. When the thermometer shows 212° F., the boiling commences; it then rises slowly to 302° F., remains at this point for some time, and finally rises to 374° F. These three boiling-points indicate three compounds; namely, a hydrocarbon, boiling at about 212° F.; chlorœnanthylene, which boils at 305°·6 F. (uncorrected); and undecomposed protochloride of œnanthylene. Their separation can only be effected by means of very tedious fractional distillations.

Chlorœnanthylene resembles protochloride of œnanthylene, possesses a similar odour, and boils at 311° F. (Boiling-point read off 305°·6; correction 5°·4). Analysis:—

	Calculated.	Found.
C^{14}	63·2	63·5
H^{13}	9·7	9·7
Cl	21·1	26·8

In chlorœnanthylene, $C^{14} H^{13} Cl$, sodium remains unaltered at ordinary temperatures. When heated, chloride of sodium and a hydrocarbon are formed. When it is treated with alcoholic solution of potash, a hydrocarbon is also formed.

From some preliminary determinations, it is not improbable that in this case the hydrocarbon, $C^{14} H^{12}$, is produced; but this the author will investigate further hereafter, as other (alcoholic radicals) may perhaps be derived from this hydrocarbon. For if $C^{14} H^{12}$, for example, combined again with chlorine, and this compound was again decomposed by alcoholic solution of potash, $C^{14} H^{8}$, isomeric or identical with toluole, and in the same way an entire series of alcoholic radicals might perhaps be obtained.

Œnanthylene, $C^{14} H^{14}$.—Sodium is thrown into protochloride of œnanthylene contained in a tubulated retort; the whole is heated and distilled, and the distillate treated again in the same manner. It forms a limpid fluid, lighter than water, which has a peculiar leek-like odour, and boils at 203° F.

Chlorœnanthylene, deprived of its chlorine by sodium, also forms a hydrocarbon. This likewise boils exactly at 203° F., and has the same odour as œnanthylene. It must, however, have the composition $C^{28} H^{26}$, as its analysis gave—

	Calculated.	Found.
C^{28} or C^{14}	86·6	86·0
H^{26} or H^{13}	13·4	13·7

But the properties of this hydrocarbon agree so exactly with those of œnanthylene, that no formula could be definitely decided on.

The experiments described prove the similar behaviour of oil of bitter almonds and œnanthole towards perchloride of phosphorus; both are converted into protochlorides of binacid alcohols, and this reaction may be expected to occur with tolerable certainty with most aldehydes.—Liebig's *Annalen*, ciii. p. 80.

On volatile Bases and Acids in Peruvian Guano. By E. Lucius.

The author has detected dimethylamine, acetic acid, and small quantities of propionic acid and formic acid in Peruvian guano. The peculiar odour of guano is consequently to be ascribed to ammonia mixed with some dimethylamine, to propionate of ammonia, and to an ætherial body which passes over in an oleaginous form when guano is distilled with dilute sulphuric acid.—Liebig's *Annalen*, ciii. p. 105.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Jan. 7, 1858. (J. P. Gassiot, Esq., Vice-President, in the Chair.)

"On the Isolation of the Radical, Mercuric Methyle. By George Bowdler Buckton, Esq., F.R.S.

Dr. Frankland has pointed out that hydrargyro-methylium, zinc-ethylium, and analogous bodies may be regarded as formed upon the type of the metallic oxides, the oxygen of which he considered was represented by methyle, ethyle, &c. The hypothetical radical hydrargyro-methylium, $C_2H_3\left\{\begin{matrix}Hg\\Hg\end{matrix}\right.$, according to this view would correspond to numerous oxides, $O\left\{\begin{matrix}Hg\\Hg\end{matrix}\right.$.

Dünhaupt and Strecker have studied and described the salts of hydrargyro-methylium and hydrargyræthylium, but chemists do not appear, hitherto, to have succeeded in reducing these bodies to the mercuric type, or in preparing the metalloids themselves.

The author has undertaken experiments with a view to the completion of this portion of their history, a brief summary of which he now offers.

Iodide of hydrargyro-methylium was prepared through the agency of sunlight, in the usual manner; and after the removal of every trace of iodide of methyle, it was intimately mixed in a mortar with finely powdered cyanide of potassium. Small charges were then introduced into flasks and distilled over the gas flame. Gaseous and solid products are formed, together with a heavy liquid, which passes into the receiver. After washing with water, and rectification over chloride of calcium, this liquid has the following properties:—

It is colourless, highly refractive to light, and almost wholly insoluble in water. When pure, it has a faint and somewhat sweetish odour. It is very combustible, and burns with a luminous flame and abundant evolution of mercurial vapour. It is very soluble in alcohol and in ether, from the former of which it precipitates on addition of water. Its boiling-point lies between 93° and 96° C, and its specific gravity is 3·069. It thus appears to have a weight greater than any known non-metallic liquid at ordinary temperature.

By analysis it gave numbers according with the formula

$$C_2H_3Hg.$$

The formation of this body is readily intelligible from the following equation, if we neglect secondary decompositions,—

$$C_2H_3Hg_2, I + KCy = C_2H_3Hg + KI + Cy + Hg.$$

The cyanogen does not, however, appear as liberated gas, but remains behind in the form of paracyanogen.

From the constitution of this substance, the name mercuric methyle is proposed. Should this appellation be accepted, Dr. Frankland's radical would be styled mercurous methyle.

To control the analysis, and further corroborate the formula, the specific gravity of the vapour was taken after Dumas's method. It was found to be 14·86. The weight represented by the formula C_2H_3Hg, divided by the experimental density, gives the quotient 7·73. Supposing the constituents of mercuric methyle condensed into one volume of vapour, the number 7·23 should have been obtained.

The theoretical density of mercuric methyle is $\frac{115}{7{\cdot}23} = 15{\cdot}9$. It is, however, more probable that the elements of this compound are condensed into two volumes, whence the formula should be doubled to $(C_2H_3)_2Hg_2$.

Mercuric methyle may also be obtained, but less readily, by employing hydrate of potassa or lime, instead of an alkaline cyanide.

In this reaction much gas is liberated.

$$2(C_2H_3Hg_2,I) + 2KOHO = C_2H_3Hg + C_2H_4 + 3HgO + HO + 2KI.$$

Mercuric methyle exhibits no tendency to unite with the electronegative elements, such as chlorine, oxygen, &c. All attempts to produce such combinations lead to the destruction of the substance. With iodine or bromine the liquid hisses as if hot metal were plunged into water. Methyle gas is liberated, and the iodide or bromide of mercurous methyle is produced:—

$$\left.\begin{matrix} C_2H_3Hg \\ C_2H_3Hg \end{matrix}\right\} + I = \underbrace{C_2H_3Hg_2\,I}_{\text{Iodide of mercurous methyle.}} + C_2H_3.$$

On the other hand, the action of concentrated sulphuric or hydrochloric acid furnishes hydride of methyle or marsh gas, with deposition of crystals of the corresponding chloride or sulphate.

$$\left.\begin{matrix} C_2H_3Hg \\ C_2H_3Hg \end{matrix}\right\} + HCl = C_2H_3Hg_2Cl + C_2H_3,H.$$

The salts of mercurous methyle, and the radical mercuric methyle, are both decomposed by the action of a dilute acid and clean zinc, into metallic mercury and gases.

Mercuric methyle furnishes with bichloride of tin a crystalline compound, which decomposes, on addition of water, into chloride of mercurous methyle and a soluble tin salt. The same chloride also is produced by the action of terchloride of phosphorus.

Mercuric methyle is a ready solvent of caoutchouc, resins, and phosphorus. It, however, has but little solvent action on sulphur.

Some interest attaches to the circumstance that iodide of mercurous methyle is easily produced by heating mercuric iodide with mercuric methyle.

Mercuric ethyle.

The author has also prepared the radical of mercuric ethyle. From its proneness, however, to decomposition at the high temperature at which the reaction is effected, he has not been able to obtain more than sufficient to make a qualitative examination of the new body. It boils at a temperature above that of water, and burns with a more lurid flame than is exhibited by mercuric methyle.

Jan. 14. (The Lord Wrottesley, President, in the Chair.)

"On some of the Products of the Destructive Distillation of Boghead Coal."—Part II. By C. Greville Williams, Esq.

In this paper the author describes the method adopted by him for the separation of the three classes of hydrocarbons forming the more volatile portion of the distillate. On treatment with bromine in presence of water, the naphtha is entirely converted into a heavy oil, containing the $C^n H^n$ series chemically, and propyle and benzole mechanically combined. The two latter may be removed by mere distillation on the water-bath. They are easily separable by fuming nitric acid, the benzole being dissolved while the propyle is untouched. The nitro-benzole obtained in this manner, on treatment by Béchamp's process, yields aniline mixed with a little toluidine, but no bases belonging to any other class.

The bromine compound (in consequence of its preparation in presence of water) could not be obtained free from oxygen. When kept for some time it separates into three layers, the upper being water faintly acidulated with hydrobromic acid, the middle bromine compound, and the lower, hydrobromic acid of 37 per cent., and the density 1·320. The bromine compounds, treated successively with alcoholic potash and sodium, undergo a curious decomposition, the original hydrocarbons, from which they were derived, being regenerated. The brominated oil from the naphtha, boiling between 71° and 77°, affords hexylene boiling at 71°, and the oil from the next homologue distilling between 82° and 88°, yields heptylene boiling at 99°. The annexed Table illustrates some of their physical properties.

Physical Properties of Hexylene and Heptylene from Boghead Naphtha.

	Formula.	Boiling-point.	Density at 18°.	Density of Volume.	
				Expt.	Theory.
Hexylene	$C^{12} H^{12}$	71°	....	3·020	2·904
Heptylene	$C^{14} H^{14}$	99°	0·718	3·320	3·386

Jan. 28. (Richard Owen, Esq., Vice-President, in the Chair.)

"On the Action of Nitrous Acid on Aniline." By A. Matthiessen, Ph.D.

On repeating the experiments of Hunt* and Hofmann†, on the action of nitrous acid on aniline, I found that the reaction does not take place exactly as these chemists state; Hunt gives the reaction as

$$\left.\begin{matrix} C_{12}H_5 \\ H \\ H \end{matrix}\right\} N + NO_3 + HO = C_{12}H_6O_2 + N_2 + 2HO.$$

Hofmann says that phenylic alcohol is not formed, but nitrophenassic acid, when binoxide of nitrogen is led into a diluted solution of the nitrate:

$$\left.\begin{matrix} C_{12}H_5 \\ H \\ H \end{matrix}\right\} N + NO_3 + NO_2 = C_{12}\left\{\begin{matrix} H_5 \\ NO_4 \end{matrix}\right\} O_2 + N_2 + 2HO.$$

This reaction, although correct in the end result, omits the intermediate stage, which is—

$$\left.\begin{matrix} C_{12}H_5 \\ H \\ H \end{matrix}\right\} N + H_2O_2 + NO_3 = C_{12}H_6O_2 + NH_3 + NO_3,$$

and then $NH_3 + NO_3 = N_2 + 3HO$.

On account of the free nitric acid, the phenylic alcohol is always converted into nitrophenassic acid. The ammonia was determined as platinum salt, and two experiments gave 43·9 and 44·1 per cent. of platinum; the theoretical quantity required is 44·2 per cent.

It appears, therefore, when nitrous acid acts on aniline, that in the first part of the reaction it causes only a substitution, and afterwards, the ammonia being attacked by it, gives off nitrogen and water.

Ammonia was obtained either by treating aniline with nitrous acid, or by the action of nitrate of potash on the chloride, or by leading the binoxide of nitrogen into a solution of the nitrate; the latter was the way generally employed. After about twelve hours' action of NO_2 on a solution of the nitrate in a water-bath, the solution was filtered from the nitrophenassic acid, and distilled with potash, the distillate treated with ether to dissolve out the aniline, redistilled in hydrochloric acid, evaporated, and the ammonia determined as platinum salt. These results have led me to try the action of nitrous acid on other organic bases, and I have already obtained from ethylaniline a base which to all appearance is ethylamine. The chloride gives off, when heated with potash, an alkaline inflammable gas, and the platinum salt resembles that of ethylamine; but the platinum determination made with it does not agree very well with that salt. I am now repeating the reaction on a larger scale, so that I shall shortly be able to see whether it is really ethylamine or not.

* Chem. Gaz. vol. viii. p. 21. † Chem. Soc. Quart. Journ. iii. 231.

THE CHEMICAL GAZETTE.

No. CCCLXXI.—April 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Air on Alkaline Arsenites.

By HENRY CROFT, University College, Toronto*.

IT is well known that a solution of arsenite of soda has been employed of late years as an important agent in volumetric analysis, especially in the determination of the value of chloride of lime. Fresenius (Chemical Gazette, No. 300) has objected to this process, that the alkaline arsenite when in solution is liable to oxidation, and that by exposure to the air a notable quantity of the arseniate is formed, which of course interferes with the accuracy of the volumetric determination.

He states that a freshly prepared solution of arsenite of soda gives the usual pale yellow precipitate with nitrate of silver, but that with a solution which has been exposed for some time, a precipitate having a brown tinge is obtained, and he affirms that nearly the whole of the arsenious acid is converted into arsenic in the course of three weeks, if the bottle in which the alkaline solution is contained be opened rather frequently. He also detected the presence of arseniate in Fowler's solution, a fact which is of some importance in a medical point of view.

On the other hand, Mohr (to whom we are indebted for most important improvements in this very elegant branch of chemical analysis), denies the oxidation of the liquor arsenicalis, and also of the arsenite of soda in presence of excess of carbonate, and by volumetric experiments with a solution of the arsenite mixed with starch and a normal solution of iodine in iodide of potassium, he proved that no change had taken place in a solution which had been kept ten months. He states that this latter solution gave, with nitrate of silver, a pure canary-yellow precipitate, without any admixture of brown.

The following experiments, without fully clearing up the difficulty, at least exhibit one of the causes of the discrepancies in the statements of the above mentioned eminent chemists.

* Communicated by the Author; having been read before the Canadian Institute, January 1858.

The formation of a pure canary-yellow coloured precipitate in a solution of an alkaline arsenite, is no proof that an arseniate is not present. If 99 parts of arsenious acid be mixed with 1 part of arsenic acid, and dissolved in potassa, the solution carefully neutralized with acetic acid and then tested with nitrate of silver, a pure yellow precipitate is produced without a trace of brown, and the same is the case if the amount of arsenic acid be increased even to 5 per cent. Beyond that quantity the brownish-red tint becomes perceptible.

But if to the solution in which the yellow precipitate has been formed, very dilute nitric acid be cautiously added, drop by drop, the arsenite of silver being more readily soluble in nitric acid than the arseniate, will dissolve first, and leave the latter with its characteristic colour. The smallest excess of nitric acid, however, dissolves the arseniate and destroys the experiment. By adding ammonia and again trying the nitric acid, we can almost always succeed in producing the red colour. That the nitric acid employed in the process exerts no oxidizing action on the arsenious acid is easily proved by using a pure arsenite, when no trace of brown coloration can be obtained.

Instead of nitric acid we may employ acetic, in which the arsenite of silver is readily soluble, but the arseniate quite or nearly insoluble. With either acid, however, it is somewhat difficult to detect the presence of the arsenic acid when it does not amount to more than 1 per cent. When 10 per cent. of arseniate is present the brownish red colour is produced immediately; with 7 per cent. the colour is fainter, and with 5 per cent. the precipitate is so nearly pure yellow that no safe conclusions can be drawn as to the presence of arsenic acid from the colour alone.

Solutions of equal quantities of arsenious acid in potassa, carbonate and bicarbonate of potassa, carbonate of soda, bicarbonate and caustic soda, were prepared twelve months ago, with a view to some experiments on this subject, but have remained untouched until the present time, the last two being unfortunately lost. They were all freely exposed to the air, but in neither of the first four cases could any brown coloration be detected on neutralizing with acetic acid, and precipitating by nitrate of silver. In all of them, however, the arseniate was readily detected by the process above described, thus confirming, as might have been expected, the results of that most accurate analyst, Fresenius.

While the oxidation of the arsenious acid was thus clearly proved, the amount converted into arsenic acid was found to be exceedingly small, and what is most remarkable is, that the sclution in bicarbonate of potassa showed a much larger proportion of arseniate than either of the others, but in no case was the quantity very large, herein differing from Fresenius' experiments.

The following experiments were made with the view of confirming Fresenius' statement with regard to the rapid oxidation of arsenite of soda: equal quantities of arsenious acid were dissolved in potassa, soda, and their bicarbonates, the latter being used in

excess. After free exposure to the air for three weeks, it was found that all the solutions gave a pure canary-yellow precipitate with nitrate of silver, but that in the case of the soda solution the presence of an appreciable quantity of arseniate could be detected by using nitric or acetic acid in the manner above mentioned. The potassa solution gave an exceedingly faint, almost imperceptible trace of arseniate; and the same was the case with the bicarbonate solutions. Portions of these liquids which had been kept in close stoppered bottles gave of course no indication of arseniate. From comparative experiments the quantity of arseniate in the soda solution was estimated at between 2 and 3 per cent., a result which differs most unaccountably from that obtained by Fresenius.

From these experiments it would appear that, contrary to Mohr's statements, oxidation does take place in solutions of alkaline arsenites exposed to the air, but that the amount of oxidation is in most cases so small as not to interfere with the employment of such solutions in accurate volumetric experiments, unless under such abnormal and unknown conditions as apparently occurred in Fresenius' experiments.

It would seem therefore advisable in preparing solutions for such purposes to adopt Mohr's suggestion, viz. to acidulate the arsenite of soda solution with sulphuric acid, and then to dilute to 1 litre (or other measure), and before using the solution to supersaturate with carbonate of soda. All oxidation would thus be prevented, as free arsenious acid in solution does not pass into arsenic acid. A solution which had been very frequently exposed to the air for the last six years, showed no trace of the latter.

[From experiments made since the above was written, it would appear that the use of acetic acid in this mode of testing is far preferable to that of nitric acid, the least excess of which dissolves the arseniate. If a considerable excess of acetic acid, containing about 20 per cent., be added to the precipitate, the arsenite dissolves, and the arseniate separates as a light flocculent matter on the surface, exhibiting very distinctly the brown colour. In this manner less than 1 per cent. can be readily detected. Experiments made on some of Fowler's solution, which had been kept two months, discovered slight traces of arseniate. It would be interesting to ascertain under what circumstances Fresenius' experiments were made; in the above, in which so very little oxidation took place, the solutions in potash and soda were made as neutral as possible.]

On Mycose, the Sugar of Ergot of Rye. By Prof. MITSCHERLICH.

By extracting ergot of rye with æther, boiling it with alcohol, evaporating the alcoholic solution, dissolving the residue in water, evaporating these solutions to the thickness of an extract, and leaving them to stand for a long time, Wiggers obtained crystals which he declared to be a peculiar sugar. Perhaps Pettenkofer had already obtained these crystals, and regarded them as phosphate of

morphia. Wiggers gave some of these crystals to Liebig and Pelouze, who analysed them; from his description and their analyses, made with a portion which was not quite pure, they co cluded that these crystals were mannite. As the form of some crystals which the author obtained from Wiggers was different from that of mannite and the other known sugars, he prepared this sugar in considerable quantity, when its peculiarity was confirmed, and as it stands in close relation to the other substances of the saccharine group, and when its properties are better known, will certainly be found more abundantly than is the case with mannite and inosite, it was submitted to an accurate examination.

This sugar is best obtained when the ergot is finely powdered and extracted with water; the filtered fluid is precipitated with basic acetate of lead, with which the sugar gives no precipitate, the excess of oxide of lead is removed from the filtered fluid by sulphuretted hydrogen, and the fluid is evaporated to the consistence of a syrup in the water-bath. If a sample leaves a residue when dissolved in water, the whole is again dissolved, filtered, and evaporated; the concentrated fluid is allowed to stand for a long time, when crystals are formed in it, and when their quantity no longer increases, the adherent fluid is removed by washing with alcohol, in which the sugar is insoluble. By repeated solution in water and crystallization, the crystals are obtained colourless and transparent, with smooth, readily measurable surfaces, and of a remarkable lustre, when the sugar is dissolved in boiling dilute alcohol, and the solution is left to cool. 2 kilogrammes of ergot gave 2 grms. of sugar; the ergot of 1856 gave no sugar in repeated experiments with variation of the processes; in one case mannite was obtained, but in this year scarcely any ergot could be collected, as hardly any was formed in consequence of the season being so favourable for the development of the rye.

The crystals have a sweet taste, and are very soluble in water; no crystals separate on the cooling of an aqueous solution containing 50 per cent. of sugar. In alcohol they are almost entirely insoluble; boiling alcohol dissolves less than one hundredth part of its weight, and most of the portion dissolved crystallizes on cooling. In æther they are insoluble.

A solution of the crystals is not precipitated by solutions of baryta and lime. When dissolved in a concentrated solution of soda and boiled therewith, the solution did not become in the least brown, even when it was exposed for several hours to a temperature of 212° F., nor did any perceptible change take place.

If the solution of the crystals be mixed with soda and sulphate of copper, a deep blue solution is obtained, which does not lose its colour or deposit any protoxide of copper; a very slight deposit of protoxide of copper took place only when it had been exposed for several hours to a temperature of 212° F.

In the first hydrate of nitric acid the sugar dissolves with a very inconsiderable evolution of heat; water separates from the solution a sticky mass, which is insoluble in water, but readily soluble in

alcohol and æther; on the evaporation of the alcohol or æther, the dissolved matter is left again in the sticky state. When heated, this body first of all melts, and then becomes decomposed with incandescence and slight detonation. If the sugar be boiled with ordinary nitric acid, it is decomposed, with formation of oxalic acid. Towards nitric acid, alkalies and sulphate of copper, therefore, this sugar behaves like cane-sugar.

In fuming, as in ordinary sulphuric acid, it dissolves without decomposition; the solution is colourless, but when it is heated to 212° F., a decomposition takes place, with production of a strong brown colour.

During crystallization the solvent fluid exerts a great influence upon the development of the crystals of this sugar, as upon similar sugars, such as sorbine; from an aqueous solution it is usually obtained with curved faces, but from a solution containing alcohol, with very beautiful smooth faces. The author has already called attention to this fact on several occasions, and indeed first with regard to the acid phosphate and arseniate of potash, which are obtained with smooth faces from a solution containing a little neutral salt; with a slight excess of acid, the inclination of the secondary planes towards one another becomes more obtuse, by as much as 1°, and with a greater excess the faces become so curved that they are no longer measurable.

The form of the crystals is a regular octahedron. When exposed for a long time to a temperature of 212° F. in a water-bath, the sugar fuses into a perfectly transparent fluid, which becomes glassy on cooling, and only grows crystalline after a considerable time; at the same time it gives off but little water, which was undoubtedly only enclosed mechanically. Heated to 266° F. in the zinc-bath, it gives off much water, and becomes inflated; at last it again becomes solid, and even when strongly heated gives off no more water; at 410° F. the hard, vesicular mass fuses, becomes brown when a little more strongly heated, and at the same time evolves an odour of caramel. Sugar that has been heated to this temperature dissolves in water with a brown colour, and its solution, evaporated in the air, furnishes crystals of unaltered sugar, with which some uncrystallizable sugar is mixed. When exposed to a higher temperature, it is completely decomposed; a spongy coal remains, which burns without residue in the air. At 212° F. it loses 9·62 per cent. The analysis gave,—

C	38·37	12	38·09
H	6·87	11	6·88
O	54·76	11	55·02

Of water of crystallization it would contain 2 atoms =9·52 per cent., so that the sugar would consist of $C^{12} H^{11} O^{11} + 2HO$.

0·7485 grm. of the sugar was dissolved in a little water, the solution poured into a glass bottle, which displaced 7·463 grms. of water, and the bottle was filled with water. The fluid weighed 7·7310 grms., so that it had a spec. grav. of 1·036; this solution

therefore contained 9·68 per cent., or 10·03 grms. of sugar in 100 cub. centims. When put into a tube 200 millims. in length, this solution rotated the plane of polarization by 34½° to the right; the same quantity of cane-sugar effects a rotation of 13⅓°, and the same quantity of dextrine one of 29⅓°; so that this sugar causes a greater rotation than any other compound of this group.

When this solution was diluted with water, mixed with about 10 per cent. of sulphuric acid, and evaporated in the water-bath to a little more than its former specific gravity, its rotatory power had undergone no change; when mixed with potash and oxide of copper, and heated, a sample gave no reduction of oxide of copper; when boiled strongly for half an hour, the rotation diminished by about 13°, and a sample mixed with potash and sulphate of copper, and boiled, effected a partial reduction of the peroxide to protoxide; when boiled for several hours, so much concentrated that a slight brown tint was produced, it rotated the plane of polarization about 10°. In these experiments the samples taken out were included in the calculation, and the same measure of fluid was always employed. This rotation nearly agrees with that of a solution of starch-sugar of corresponding strength.

After the sulphuric acid had been got rid of with carbonate of baryta, and the filtered, evaporated fluid had been set aside for a considerable time, it solidified almost completely into verrucose crystals, the solution of which was set in fermentation by yeast as quickly as starch-sugar. By long boiling with dilute sulphuric acid, therefore, the sugar of ergot is converted into starch-sugar.

As this sugar occurs in a fungus (*μῦκος*), and belongs to the group of cellulose, glycose, and dulcose, the name *mycose* appears to be the most suitable.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 469.

On Alcoholic Fermentation. By M. Pasteur.

The author adds the following new results to those which he communicated to the Academy of Sciences on a former occasion*. He has found that succinic acid is one of the normal acids of alcoholic fermentation, that is to say that there is never any alcoholic fermentation without the formation of a certain quantity of succinic acid at the expense of the sugar. The amount of succinic acid rises to at least ½ per cent. of the sugar fermented.

The presence of this acid may be easily proved, even when only a few grammes of material are operated upon. When the fermented liquid is evaporated, rendered neutral, and precipitated by a silver-salt, the succinate washed and decomposed by sulphuretted hydrogen, furnishes crystals of succinic acid on evaporation. Or if the fermented liquid be treated repeatedly with æther, crystals of succinic acid will be deposited by degrees on the walls of the vessel. When the crystallization does not take place, that is when the succinic

* See Chem. Gaz., February 15, 1858.

acid remains dissolved in the syrup of lactic acid left by the æther after its evaporation, it is sufficient to saturate the two acids by lime. The succinate of lime, being insoluble in weak alcohol, is easily separated from the lactate. If this acid should ever become of any service in medicine, it might probably be obtained in abundance from the refuse of distilleries.

The author also ascertained the presence of succinic acid in wine by evaporation and treatment with æther. The syrup of lactic acid left by the evaporation of the æther, furnished a very appreciable quantity of succinic acid.—*Comptes Rendus*, Jan. 25, 1858, p. 179.

On Double Nitrosulphurets, a new Class of Salts. By M. Roussin.

It is a question whether the latent state of iron in the prussiates is the result of the presence of cyanogen or of the peculiar mode of grouping of the molecule. The author considers the latter to be the only probable hypothesis, for he has just discovered a new series of bodies in which this latent state of iron occurs in the highest degree, although they contain no trace of cyanogen.

If a soluble proto- or sesquisalt of iron be dropped and stirred into a mixture of an alkaline nitrate and hydrosulphate of ammonia, and the liquid be filtered after boiling for a few minutes, fine, black, brilliant prismatic needles are deposited on cooling, to which the author attributes the formula

$$FeS, NO^2 + Fe^2 S^3, NO^2 + SH.$$

This body the author calls *binitrosulphuret of iron*. It is soluble in alcohol and water, and deliquescent in vapour of æther. The form of the crystals is the oblique prism with a rhombic base. They are decomposed at about 266° F., evolving deutoxide of nitrogen and sulphurous acid, and leaving a residue of sulphuret of iron.

When boiled with a solution of caustic soda, this body disengages torrents of ammonia, deposits crystalline sesquioxide of iron, and becomes converted into a new body with the formula

$$Fe^2 S^3, NO^2, 3NaS.$$

This new compound crystallizes in large crystals arranged in troughs. It is very soluble in water and alcohol, but insoluble in æther, and gives rise to phænomena of double decomposition with metallic solutions.

Treated with a dilute acid, it deposits a reddish body which is insoluble in water, soluble in alcohol and æther, of the formula

$$Fe^2 S^3, NO^2, 4HS.$$

This is the *sulphuretted nitrosulphuret of iron*. It decomposes gradually, setting free its sulphuretted hydrogen. If the liquid in which it is suspended be boiled, all the sulphuretted hydrogen quits it tumultuously, and it is finally converted into a black, heavy powder, insoluble in water, alcohol and æther, of which the formula is

$$Fe^2 S^3, NO^2.$$

This nitrosulphuret of iron dissolves entirely in sulphuret of sodium, and gives a new salt,—

$$Fe^{2}\,S^{3},\ NO^{2},\ NaS,\ HO,$$

called *nitrosulphuret of iron and sodium*. It crystallizes in red prismatic needles, of an extraordinarily intense colour. It is very soluble in water, alcohol, and æther; insoluble in chloroform and sulphuret of carbon. With metallic solutions it gives very marked phænomena of double decomposition. Many of these new salts are immediately decomposed. Many are stable, and although insoluble in water, soluble in alcohol and æther. The new metal is merely substituted for the sodium.

In all these compounds the molecule of iron remains insensible to the characteristic reactions. Thus hydrosulphate of ammonia, yellow and red prussiates, tannine, and potash, have no action upon them.

The question to what series these salts belong is answered by the following experiments:—

1. If a nitrosulphuretted compound be digested for a few minutes with simple cyanide (cyanide of potassium or mercury), all the sulphur of the compound passes to the state of sulphuret in combination with the new metal, whilst the cyanogen converts the nitrosulphuret into nitroprussiate.

2. If a current of sulphuretted hydrogen be passed into a solution of nitroprussiate of soda until the complete destruction of the compound, and the liquid is evaporated after filtration, it is found converted into nitrosulphuret of iron and sodium.

3. A mixture of nitrite of potash and perchloride of iron is divided into two parts. An alkaline cyanide is poured into one, and an alkaline sulphuret into the other, and both are filtered. The first contains considerable quantities of nitroprussiate; the second appears to be entirely converted into nitrosulphuret.

The double nitrosulphurets are therefore related to the nitroprussiates, by a parallel mode of production and an analogous composition. The sulphur replaces the cyanogen, and actually plays its part. The latent state of the iron is sufficient to ally these curious compounds with the prussiates.—*Comptes Rendus*, Feb. 1, 1858, p. 224.

On the Chinese Yellow-pods. By F. Rochleder.

The colouring matter of the Chinese yellow-pods is a conjugate hydrate of carbon, according to the experiments of Mayer. The hydrate of carbon which is separated by the action of muriatic acid, is crystallized sugar. In all probability the colouring matter of the yellow-pods is identical with that of saffron, with which it has all its reactions in common. The colouring matter of saffron was analysed by Quadrat; it appears not to have been perfectly pure. The pure colouring matter of the yellow-pods does not dye any more than the ruberythric acid of madder. But the product of

decomposition dyes a fine golden-yellow colour. This explains the want of success of the attempts at dyeing with yellow-pods in Europe, and the employment of this material in dyeing in China.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxiv. p. 41.

On Amyloglycol. *By* A. Wurtz.

The author has already several times called the attention of chemists to a new series of organic compounds, which he calls *glycols*. In their general properties these compounds approach the ordinary alcohols, but are never liable to be confounded with them. They are distinguished from them by the fact, that in forming neutral æthers they combine with 2 equivs. of a monobasic acid, that is to say, they are *diatomic*. The author now asserts that there is a glycol to correspond with each mono-atomic alcohol.

He has hitherto obtained four glycols, namely:—

Ordinary glycol ...	$C^4 H^6 O^4$,	corresponding with alcohol	$C^4 H^6 O^2$
Propyloglycol ...	$C^6 H^8 O^4$,	„	„	propylic alcohol	$C^6 H^8 O^2$
Butyloglycol	$C^8 H^{10} O^4$,	„	„	butylic alcohol	$C^8 H^{10} O^2$
Amyloglycol	$C^{10} H^{12} O^4$,	„	„	amylic alcohol	$C^{10} H^{12} O^2$

Thus the glycols only differ from the corresponding alcohols by their containing 2 equivs. more oxygen.

They were all obtained by synthesis:—glycol, with olefiant gas, $C^4 H^4$; propyloglycol, with gaseous propylene, $C^6 H^6$; butyloglycol, with butylene, $C^8 H^8$; and amyloglycol, with amylene, $C^{10} H^{10}$.

To obtain amyloglycol, amylene was converted into bromide, $C^{10} H^{10} Br^2$, and the bromide treated with acetate of silver. Diacetic amyloglycol was formed in accordance with the following equation:—

$$\underbrace{C^{10} H^{10} Br^2}_{\text{Bromide of amylene.}} + 2 \underbrace{\left\{ \begin{matrix} C^4 H^3 O^2 \\ Ag \end{matrix} \right\} O^2}_{\text{Acetate of silver.}} = \underbrace{\left\{ \begin{matrix} C^{10} H^{10} \\ (C^4 H^3 O^2)^2 \end{matrix} \right\} O^4}_{\text{Diacetic amyloglycol.}} + 2 Ag Br.$$

Diacetic amyloglycol is a colourless, neutral liquid, insoluble in water, and decomposable with the greatest ease by alkalies, into acetic acid and amyloglycol. It contains—

	Found.		Calculated.	
C	57·03	57·18	18	57·44
H	9·02	9·06	16	8·51
O	..	..	8	34·05

When treated with the proper quantity of dry pounded hydrate of potash, it was decomposed exactly into acetic acid and amyloglycol. The latter is volatile, and was separated by distillation on the oil-bath.

When pure, amyloglycol is a perfectly colourless, very syrupous liquid, of a bitter taste. It does not solidify at 4° F., but becomes so viscous, that the tube containing it may be turned upside down without its running. It has no rotatory power. Its density at 32° F.

is 0·987. It boils at 350°·6 F., and distils without alteration. Its boiling-point is lower than that of propyloglycol, which passes at 377°·6 F.; and this boils at a lower temperature than glycol. These facts constitute a singular exception to the law of boiling-points. The composition of amyloglycol is expressed by the formula

$$C^{10}H^{12}O^4 = \left\{ \begin{matrix} C^{10}H^{10} \\ H^2 \end{matrix} \right\} O^4.$$

This formula is deduced from the following analysis:—

	Found.		Calculated.
C	57·77	10	57·69
H	11·67	12	11·53
O	..	4	30·78

Amyloglycol is soluble in all proportions in water, alcohol, and æther. When mixed with platinum black and exposed to the air, it rapidly becomes acidified. The acid thus produced forms with lime a salt which is very soluble in water and alcohol. It probably contains $C^{10}H^{10}O^6$. From this composition the acid would be a new homologue of lactic acid.

Nitric acid acts upon amyloglycol with great energy. The products of the reaction are oxalic acid, and a syrupous acid, which forms with lime a salt which is very soluble in water and alcohol, but insoluble in æther. It differs from lactic acid.—*Comptes Rendus*, February 1, 1858, p. 244.

On Caprylic Aldehyde, and Caprylic Alcohol. By G. Städeler.

The distillation-product of the alkaline ricinoleates has been frequently investigated, and has been stated by some to be caprylic, by others to be œnanthylic alcohol. Limpricht denied that an alcohol was formed, and asserted that the body in question was caprylic aldehyde, but agreed with others in finding that its boiling-point was 352° F. Bouis found that the product formed was caprylic alcohol, or caprylic aldehyde, according as the conditions were varied. By the dry distillation of neutral ricinoleate of potash, caprylic aldehyde, and an amorphous acid of the composition $C^{20}H^{18}O^4$, are formed; when ricinoleic acid is rapidly distilled with excess of potash, caprylic alcohol and sebacic acid are the products. Both substances, caprylic alcohol and caprylic aldehyde, are simultaneously obtained when ricinoleic acid is distilled with excess of potash at a temperature not exceeding 437° F. to 446° F.

It is still unexplained why, when castor oil is distilled, œnanthal and no caprylic aldehyde should be formed. To clear up this point the author undertook the investigation.

When dry ricinoleate of soda is carefully distilled, and the distillation stopped when the mass begins to froth up, a clear distillate is obtained, which solidifies when shaken with bisulphite of soda. When this compound is treated with soda, a body is separated which has the boiling-point and all the properties of œnanthal. There remains behind with the soda the same acids that are formed in the simple distillation of castor oil.

To study the decomposition of ricinoleic acid by excess of alkali, the author prepared an intimate mixture of the soda salt with excess of hydrate of soda, by mixing the former with a known quantity of a solution of the latter, and carefully evaporating to dryness. The mixture on analysis was found to contain 33·3 per cent. soda, or 43·3 per cent. hydrate of soda. This mixture was distilled in quantities of a pound at a time, in a small copper retort, the bottom of which was covered to a height of $\frac{3}{4}$ of an inch by this quantity. In this manner a regular and uniform heat could be applied. The decomposition was very easy, and the distillate, which consisted of water and an oily layer, was colourless. The distillation was stopped as soon as it became necessary to apply a high heat in order to bring over more distillate. The residue was white and pulverulent: it contained a large quantity of sebacic acid.

The oily distillate separated from the water and dried, was rectified. It began to distil at 302° F., but boiled principally at 352° F. The distillates 302° to 347° F., and 347° to 361° F. were collected separately, and treated with bisulphite of soda, and as both solidified to a crystalline mass, they were united, allowed to stand 24 hours, pressed free from water by linen, and then pressed between blotting-paper in the hydraulic press.

I. *The product which did not combine with bisulphite* was extracted from the papers by distillation with water, then dried over chloride of calcium, and rectified. By far the greater portion distilled between 350° to 352° F. To purify it, this was again treated with bisulphite of soda, by which a small quantity of gelatinous flakes were separated, then treated with soda, washed, dried, and rectified. It boiled at 350° to 351° F., and on analysis gave numbers leading to the formula $C^{14} H^{16} O^2$.

		Calculated.	Found.	
14 equivs. Carbon	84	72·42	72·27	72·40
16 equivs. Hydrogen	16	13·79	13·56	13·55
2 equivs. Oxygen	16	13·79	14·16	14·05

The body is thus œnanthylic, and not caprylic alcohol. It is a clear but somewhat thick liquid, with an odour resembling œnanthal. Its spec. grav. is 0·819. It is neutral, but becomes acid in contact with platinum black. It dissolves in concentrated sulphuric acid, forming sulphœnanthylic acid.

2. *The combination with bisulphite of soda* was purified by repeatedly mixing it with alcohol to a paste and pressing. When gently warmed with water, an oily layer separated which did not perceptibly increase on the addition of carbonate of soda. This was collected, dried over chloride of calcium, and rectified. Its boiling-point was found to be 340° F. On analysis numbers were obtained which are expressed by the formula $C^{16} H^{16} O^2$.

		Calculated.		Found.
16 equivs. Carbon	96	75·0		74·95
16 equivs. Hydrogen	16	12·5		12·54
2 equivs. Oxygen	16	12·5		12·51

This body has the composition of caprylic aldehyde, but it has none of the properties of an aldehyde. It is not oxidized even by boiling with bichromate of potash and sulphuric acid; it is not changed by boiling potash, and it forms no compound with ammonia. It reduces oxide of silver, but this property is common to the cetones.

From its composition it might be the cetone of œnanthylic acid, and in order to compare the substances the author prepared this body by distilling acetate and œnanthylate of soda:—

$$\left.\begin{matrix} C^4 H^3 O^2 \\ Na \end{matrix}\right\} O^2 + \left.\begin{matrix} C^{14} H^{13} O^2 \\ Na \end{matrix}\right\} O^2 = 2NaO\,CO^2 + \left.\begin{matrix} C^{14} H^{13} O^2 \\ C^2 H^3 \end{matrix}\right\}$$

Acetate of soda. Œnanthylate of soda. Methylœnanthal.

An oily distillate was obtained, which was rectified, shaken with bisulphite of soda and pressed, then treated with a little alcohol, and again pressed. It was then treated with water and carbonate of soda, the oily layer which separated dried over chloride of calcium, and rectified. It boiled at 340° F., and gave on analysis numbers which agree with the formula of methylœnanthal, or the acetone of œnanthylic acid.

	Calculated.		Found.
16 equivs. Carbon	96	75·0	74·78
16 equivs. Hydrogen	16	12·5	12·47
2 equivs. Oxygen	16	12·5	12·75

Methylœnanthal is a colourless, mobile liquid, boiling at 340° to 341° F., with an odour like oil of rue, and a taste like that of the fresh plant. It is insoluble in water, but miscible in alcohol and æther in all proportions. It is neutral, and does not become acid even on lengthened exposure to the air.

By the distillation of castor oil with excess of potash, there is formed therefore neither caprylic aldehyde nor caprylic alcohol, but œnanthylic alcohol, and methylœnanthal. Their formation may be thus expressed:—

$$C^{36} H^{34} O^6 + 2(KO\,HO) = 2KO, C^{20} H^{16} O^6 + C^{16} H^{16} O^2 + 4H$$

Ricinoleic acid. Sebacate of potass. Methylœnanthal.

$$C^{36} H^{34} O^6 + 2(KO\,HO) = 2KO, C^{20} H^{16} O^6 + C^{14} H^{16} O^2 + C^2 H^4$$

Ricinoleic acid. Sebacate of potass. Œnanthylic alcohol. Marsh-gas.

It is possible that œnanthylic alcohol may be formed by a secondary process, the action of alkali on the sebacate, for the researches of Calvi and of Petersen* have shown that œnanthylic alcohol is formed in the distillation of sebacate of lime.—*Journal für Prakt. Chemie*, Dec. 21, 1857.

On Saponine. *By* M. von Payr.

In his investigation of the seeds of the Horse-chestnut, Rochleder found a beautifully crystallized, colourless, silvery substance, which forms a principal constituent of the seeds, inasmuch as the other

* Chem. Gaz., Jan. 15, 1858.

non-crystalline constituents stand in a very simple relation to it. This substance is a conjugate compound, giving products of decomposition with alkalies and acids, which stand in a remarkable and simple relation to chinovic acid. It thus became necessary to examine again saponine and caincic acid, which has the same percentage composition as the substance from the seeds of the Horse-chestnut, and also chinovic acid. The author has undertaken the investigation of saponine, and has obtained from it, by the action of potash, a beautifully crystallized acid, together with an amorphous substance, which latter is again decomposed by muriatic acid into two products. The experiments of Schnedermann are completely confirmed, and all uncertainty which could not be got rid of either by Rochleder and Schwarz*, or by the persevering researches of Bolley†, entirely disappears.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxiv. p. 42.

Researches upon Isomeric Bodies. New Derivatives of Oil of Cloves. By AUGUSTE CAHOURS.

Almost every day reveals the existence of new compounds, which, formed of the same elements, combined in the same proportions, possess the most dissimilar properties. Sometimes these bodies, identical in composition, possess a different equivalent,—such are the various carburets of hydrogen related to olefiant gas, and the hydruret of salicyle in relation to hydruret of benzoyle. Sometimes they possess the same chemical equivalent and vapour equivalent,—such is hydruret of salicyle in relation to benzoic acid. The former are called *polymeric*, the latter *isomeric* bodies. To explain this curious property, it is supposed that in isomeric bodies the elementary molecules mutually occupy different positions, but this pure speculation required experimental demonstration.

In a recent paper on hydruret of salicyle, the author showed, that, by the reciprocal action of this body and the chlorides of the organic radicals, substances were produced presenting perfect isomerism with the corresponding compounds furnished by benzoic acid, but differing from them completely in their neutrality. Not only do these bodies not combine with, or become decomposed by alkalies, but they even resist the action of solid potash and anhydrous baryta.

With the object of making a comparative study of the established isomeric bodies, the author has carefully investigated eugenic acid (the acid portion of the essential oils of cloves and pimento), which, according to the analyses of Dumas and Stenhouse, is identical in composition with cuminic acid.

The chlorides of the organic radicals act upon eugenic acid with the aid of a gentle heat. As with its isomer an abundant evolution of muriatic acid is observed, but no double acid is obtained; there is formation of crystallized bodies, insoluble in solution of potash, even when concentrated and hot, but completely decomposable by

* Chem. Gaz. vol. xii. p. 1. † *Ibid.* p. 330.

solid hydrate of potash, which sets free eugenic acid and the acid corresponding with the chloride employed. Eugenic acid, therefore, like hydruret of salicyle, by its reaction upon organic chlorides, forms compounds isomeric, but not identical with those furnished by cuminic acid; they are characterized by a perfect neutrality. But whilst in the case of hydruret of salicyle the elements of the compound fuse together so intimately that they cannot be reproduced by means of reagents, those formed by eugenic acid obey the laws which govern the æthers, the fatty bodies, the amides, glucosides, &c.

Hydruret of salicyle being capable of forming definite compounds with bases, as well as the derivatives by substitution formed by the action of chlorine and bromine, we cannot understand how the products resulting from the mutual action of this body and the chlorides of the organic radicals present a complete neutrality, without supposing that in the two cases it is not the same hydrogen that is replaced.

Only 1 equiv. of hydrogen in hydruret of salicyle being capable of replacement by metals, whilst the others may be replaced by chlorine or its analogues, the composition of this product may be expressed as follows:—

$$C^{14} H^{5} O^{4}, H.$$

If we suppose that chlorine and bromine in acting upon this substance form

$$C^{14} H^{4} ClO^{4}, H,$$
$$C^{14} H^{4} BrO^{4}, H,$$

we shall easily understand how these derivatives play the same part as the original substance, which could not be the case if their composition were

$$C^{14} H^{5} O^{4}, Cl,$$
$$C^{14} H^{5} O^{4}, Br.$$

If the same hydrogen were replaced by the groups acetyle, benzoyle, cumyle, &c., there would be no reason why the functions of the new compounds should not be perfectly analogous.

Eugenic acid behaves towards these radicals exactly in the same way as hydruret of salicyle, and furnishes a series of well defined products, represented by the formulæ—

$C^{34} H^{6} O^{6}$, benzeugenyle,
$C^{36} H^{18} O^{6}$, tolueugenyle,
$C^{40} H^{22} O^{6}$, cumeugenyle,
&c. &c. &c.

These compounds, which crystallize with the greatest ease, are perfectly neutral, and undergo no alteration by long boiling either with a dilute solution of caustic potash, or with muriatic acid. When heated with hydrate of potash, they become most distinctly split, fixing the elements of water and reproducing eugenic acid and benzoic, cuminic acid, &c. This property, and their mode of production, approximates these bodies to the true æthers.

If the hydrogen in an acid, which may be eliminated by metals, be replaced by methyle, æthyle, or any other group, neutral products are obtained; thus, with acetic acid, we get the

Normal acid .... $C^4 H^3 O^4$, H.
Metallic acid .... $C^4 H^3 O^4$, M.
Acetate of methyle $C^4 H^3 O^4$, Me.
Acetate of æthyle $C^4 H^3 O^4$, Ae.

If, on the contrary, the hydrogen of the radical itself be replaced, the compound remains acid. Example, normal acetic acid and the monochlorinated, bichlorinated and trichlorinated acids.

These substitutions of simple bodies, or of certain groups, for hydrogen in organic compounds, according to the particular form in which this hydrogen exists in the compound, gives rise to some of the most curious cases of isomerism, the chemical properties of the derivatives sometimes differing most completely. Such are formiate of methyle and acetic acid, isomeric bodies, both of which may be regarded as derived from formic acid by the substitution of 1 equiv. of methyle for 1 equiv. of hydrogen, with the difference that in the former case the basic hydrogen is replaced by methyle, whilst in the second it is the hydrogen of the radical. Hence the constitution of these various products may be expressed as follows:—

Normal formic acid.... $C^2 HO^4$, H.
Formiate of methyle .. $C^2 HO^4$, $(C^2 H^3)$.
Acetic acid ..... $C^2 (C^2 H^3) O^4$, H.

As the second may be obtained by the action of hydriodic æther upon formiates, the third would probably be produced by that of chloroformic acid upon zincomethyle; thus

$$C^2 HO^4, M + C^2 H^3 I = MI + C^2 HO^4, (C^2 H^3)$$
$$C^2 ClO^4, H + C^2 H^3 Zn = Zn Cl + C^2 (C^2 H^3) O^4, H.$$

The action of chloroformic acid, which we may justly suppose to exist in the oxychlorocarbonic æthers, upon zincæthyle, zincamyle, &c., would then enable us to obtain all the other terms of the formic series.

The very numerous and diverse organic compounds which are capable, like alcohol, of exchanging hydrogen for binary or ternary groups, to form bodies analogous to the æthers, cannot however be assimilated to alcohol, as has recently been attempted. Alcohol and its congeners have perfectly distinct characters, and if we approximate to this compound all the substances which satisfy the preceding conditions, we should be led to arrange in this category, the acids, the sugars, and all their analogues, the amides, &c., which cannot be done rationally.—*Comptes Rendus*, Feb. 1, 1858, p. 220.

On Compounds of Guanine with Hydrobromic and Hydriodic Acids. *By* D. G. Kerner.

Hydrobromic and hydriodic acids dissolve guanine with ease when heated. On cooling, the compounds analogous to muriate of guanine separate in a crystalline form.

Hydrobromate of Guanine, $3(C^{10}H^5N^5O^2, HBr)+7HO$, forms yellowish-white, prismatic needles, which effloresce below 212° F. Above 356° F., the salt becomes inflated, but it is only when the heat is increased that the hydrobromic acid separates.

Hydriodate of Guanine, $3(C^{10}H^5N^5O^2, IH)+7HO$, forms yellowish-white, prismatic needles, rather difficult of solution in pure water, insoluble in hot water. They acquire a yellow colour under the influence of light and heat. From the concentrated mother-liquor, which becomes of an orange colour, an acid hydriodate separates, but is decomposed even by desiccation.—Liebig's *Annalen*, ciii. p. 268.

On Aldehyde-ammonia. By Prof. von Babo.

For the preparation of the aldehyde used in his investigation, the author employed Dobereiner's original process of the slow combustion of alcohol by a porous body. Instead of platinum-black, von Babo used oxide of chromium prepared by igniting chromate of ammonia; and he constructed an apparatus by which the slow combustion could be easily set up, regulated, and maintained for any length of time, and the products of the combustion collected. But it does not seem, and the author does not state, that this process has any advantage over those at present in use.

Three views prevail as to the constitution of aldehyde. Liebig considered it as hydrated oxide of acetyle, C^4H^3O, HO, assuming in it a radical C^4H^3; Kolbe assumed in it the radical C^2O^2 combined with C^2O^3, $\left.\begin{matrix}C^2H^3\\H\end{matrix}\right\}C^2O^2$; and the modern French and English school view it as a hydrogen compound of the radical $C^4H^3O^2$: on the latter view it has a formula analogous to bitter almond oil,—

$$\left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}, \qquad \left.\begin{matrix}C^{14}H^5O^2\\H\end{matrix}\right\}.$$

Aldehyde. Hydride of benzoyle.

The author hoped that the decomposition of aldehyde-ammonia might give some clue to its composition. Unfortunately, however, the products formed have properties which rendered it impossible to examine them so accurately as could be desired.

Aldehyde-ammonia heated for some time in a strong sealed tube to 120° C. disappears, and in its place are found two layers of liquid, of which the lower is brown and viscous, and the upper swims like an æther upon it. On opening the tube, ammonia is given off, and the upper layer becomes much diminished in quantity. The separation of these two liquids by distillation was attended with great difficulties, owing to the violence with which it boiled, which was in one case so great as to break the retort. A better separation was effected by distilling the liquid in bent glass tubes, such as are used in the condensation of gases, and cooling one of the legs in

ice. But even in this case the distillate was often rendered impure by the residue boiling over, or the tubes exploded with a loud report. The separation was only effected at 200° C.

The distillate consists of an aqueous solution of ammonia; traces of other bases, which could not however be isolated from their small quantities; and of traces of an oily neutral liquid which smelt like Dippel's oil.

The residue, freed as much as possible from ammonia, contains a very changeable base which has properties similar to Natanson's acetylamine, and like it can with difficulty be purified. It is obtained as an uncrystallizable, brownish mass, of feeble basic reaction, soluble in water and alcohol, forming with sulphuric acid a compound which separates as a brown syrup: it is precipitated by bichloride of platinum in brown caking flakes, and forms with gallic and chromic acids brown resinous precipitates.

Its deportment towards bichloride of platinum appeared best fitted to establish its constitution. The residue, dissolved in the least quantity of hydrochloric acid, was mixed with bichloride of platinum, the precipitate carefully washed with water, dried, and analysed.

The mean of the analytical determinations gave numbers corresponding to the formula $C^{20} H^{15} NO Pt Cl^3$.

	Calculated.	Found.
C^{20}	33·1	33·6
H^{15}	4·2	4·4
N	3·9	4·2
O	2·2	
Pt	27·2	27·4
Cl^3	29·4	

Assuming that this base combines with hydrochloric acid and chloride of platinum, as does oxide of ammonium, its formula would be $C^{20} H^{15} NO^2$.

Another portion of the basic substance was purified by repeated precipitation of the sulphate from alcohol, solution in water, decomposition of the salt by baryta, evaporation, solution in alcohol, and was then treated with hydrochloric acid and bichloride of platinum. The appearance of the substance was similar to that of the one above described, but the analyses exhibited another composition which was best expressed by the formula $C^{16} H^{13} NO^2 Pt Cl^3$.

	Calculated.	Found.
C^{16}	28·6	28·25
H^{13}	3·9	4·35
N	4·2	4·3
O	2·4	
Pt	29·3	28·7
Cl^3	31·7	

Assuming that water, ammonia, and the first base are the original products of the action from which the other bodies, together with

traces of formic and acetic acids, arise as secondary products, its decomposition would be expressed by the equation

$$5(NH^4\,C^4\,H^3\,O^2) = C^{20}\,H^{15}\,NO^2 + 4NH^3 + 8HO,$$

Aldehyde-ammonia. Base.

and the constitution of the new body would be deduced from the type $NH^4, C^4\,H^3\,O^2$, in which the 4 equivs. of hydrogen in the ammonium were replaced by $C^4\,H^3$,—

$$\left.\begin{matrix} C^4\,H^3 \\ N\,C^4\,H^3 \\ C^4\,H^3 \\ C^4\,H^3 \end{matrix}\right\} C^4\,H^3\,O^2 = C^{20}\,H^{15}\,NO^2.$$

By treatment with sulphuric acid and baryta the group $C^4\,\bar{H}^3\,O^2$ is decomposed, and replaced by 1H and 2O; the second body is formed on the type hydrated oxide of ammonium—

$$\left.\begin{matrix} C^4\,H^3 \\ N\,C^4\,H^3 \\ C^4\,H^3 \\ C^4\,H^3 \end{matrix}\right\} OHO = C^{16}\,H^{13}\,NO^2.$$

The first body might be considered as acetoxytetracetylammonium, or oxide of acetyloxytetracetylammonium, the second would be hydrated oxide of tetracetylammonium.

The formation of these bodies is so far important, that it is difficult to reconcile therewith the existence of a methyle compound in aldehyde-ammonia.—*Journal für Prakt. Chemie*, vol. lxxii. p. 88.

ANALYTICAL CHEMISTRY.

Determination of Copper by Permanganate of Potash.

By A. Terreil.

Schwarz and F. Mohr have already proposed two methods of determining copper by permanganate of potash. Both these chemists commence by converting the copper, dissolved in an acid, into potassio-tartrate of copper, then precipitating it by glucose in the form of protoxide, which is separated by filtration, and washed with care.

Schwarz treats the protoxide thus obtained with a solution of perchloride of iron, mixed with muriatic acid; by this means it is changed into perchloride of copper, converting a portion of the perchloride of iron into protochloride, which is determined by permanganate of potash, and shows the amount of copper which has reacted.

F. Mohr dissolves the protoxide in muriatic acid, adding chloride of sodium to the liquid, by which a double chloride of sodium and protochloride of copper, soluble in water, is produced. He then, starting from the property possessed by the protosalts of copper, of

becoming converted into salts of the deutoxide under the influence of permanganate of potash, determines the quantity of copper contained in the liquid, with a normal solution of the latter salt.

The author remarks that in these two processes the copper must first be separated from its solution in the form of protoxide, and that this might be weighed and the amount of copper deduced from it without having recourse to a second operation.

C. Mohr has also given a process which consists in precipitating the copper from its solutions by metallic iron, which takes the place of the copper in the state of protoxide; the quantity of iron dissolved is then determined by permanganate of potash, and from this the amount of copper is deduced. In this method the liquids must be slightly acid, to avoid the formation of subsalts of iron which have no action upon the permanganate; under these circumstances a certain quantity of iron may be dissolved by the excess of acid, and give rise to errors.

The author's method, which is rapidly executed, and furnishes very exact results, consists in,—

1. Dissolving the copper, alloy or cupreous substance in an acid; if nitric acid be employed, it may be driven off completely by treating with concentrated sulphuric acid, which converts the nitrates into sulphates.

2. Rendering the liquid ammoniacal; if precipitates be formed, they are separated by filtration.

3. Boiling the ammoniacal liquid with sulphite of soda or any other alkaline sulphite, until it is deprived of colour.

4. Pouring into the decolorized liquid a slight excess of muriatic acid, and boiling it to drive off the sulphurous acid.

5. Treating the liquid diluted with water with solution of permanganate of potash, previously tried with a known weight of pure copper treated as above.

Fifteen or twenty minutes are sufficient for an analysis. The strength of the solutions of permanganate was determined by operating upon different weights of pure copper obtained by galvanic action, and the author always obtained numbers exactly corresponding with the quantities of copper employed.

The following are the results of analyses of well-known compounds of copper:—

0·122 gr. of pure copper require 84 divisions of the normal solution.

Compounds analysed.	Weight. gr.	Number of divisions of solution.	Numbers found in hundredths.	Numbers calculated from formulæ.
Protoxide of copper ..	0·162	100	89·64	88·80
Deutoxide of copper..	0·275	151	79·74	79·86
Oxychloride of copper	0·232	95	59·43	60·22
Sulphate of copper ..	0·443	77	25·23	25·42
Cyanomercurate of ammoniaco-chloride of copper	0·496	27	7·9	8·9?

Thus the copper-salts are completely reduced to the state of protoxide by the alkaline sulphites, but only in the presence of ammonia; in the liquids thus treated the copper occurs in the state of a double proto-salt which is brought again to the maximum and decolorized by the permanganate of potash, so that a drop of this reagent added in excess indicates the conclusion of the operation by the violet rose-colour which it communicates to the liquid. The proto-salt of copper in becoming converted into a per-salt under the influence of the permanganate, gives the liquid a blue colour, which is weak in proportion as the liquid is more diluted.

It is very important to expel the nitric acid which may be in the liquid completely, as this acid forms *aqua-regia* with the muriatic acid, when the solution is boiled to drive off the sulphurous acid, and brings the copper again to the maximum state of oxidation.—*Comptes Rendus*, February 1, 1858, p. 230.

New Mode of Analysing Milk by Means of Normal Fluids.
By E. Monier.

If mineral chameleon be dropped into milk diluted with water and acidulated, the fine colour of the chameleon immediately disappears, as would that of a protosalt of iron under the same circumstances. This decoloration is due to the caseine and albumen of the milk; the butter and lactine have no deoxidizing action.

Determination of Caseine.—Two normal solutions are used, one of caseine, the other of albumen, each containing 2 per cent. of those substances. The volumes V and v of mineral chameleon, required to produce in these liquids a permanent and equally intense tint, are determined. These volumes, V and v, being thus proportional to the caseine, this substance is determined by a simple proportion; if the milk contains albumen, the volume V corresponds with the caseine and albumen; the volume V′ decolorized by albumen must therefore be determined, when $V - V'$ represents the exact volume decolorized by caseine.

Determination of Albumen.—10 cub. cent. of milk are brought to a temperature of 113°—122° F. A drop of dilute acetic acid perfectly coagulates the caseine and butter, and the albumen remains dissolved; the whole is filtered, the washing waters are collected in a large vessel, the liquid which contains the albumen is acidulated, and the volume V′ of chameleon decolorized by it is determined; the same operation is performed upon 10 cub. cent. of the normal solution of albumen, when the albumen of the milk is determined by a proportion.

Determination of Butter.—The mixture of butter and caseine, collected upon a filter from 10 cub. cent. of milk, is dried. The weight P of the dried mixture is ascertained; deducting from this the weight p of the caseine previously ascertained, the difference is the butter.—*Comptes Rendus*, February 1, 1858, p. 236.

THE CHEMICAL GAZETTE.

No. CCCLXXII.—April 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Chemical Equivalents of Barium, Strontium, and Lead. By C. MARIGNAC.

Equivalent of Barium.

SEVERAL chemists have occupied themselves with the determination of the equivalent of barium.

Berzelius found that 100 parts of chloride of barium precipitate 138·06—138·08, mean 138·07 of chloride of silver. The equivalent of barium calculated from this result, assuming 108 for silver and 35·5 for chlorine, would be 68·43.

Pelouze* introduced a slight modification into the method of Berzelius, which renders it more simple and capable of great precision. It consists in weighing nearly equivalent weights of chloride of barium and silver, dissolving the silver, adding the chloride to it, and then determining by means of normal fluids what amount of silver it is necessary to add in order to render the precipitation complete. He found that 100 of chloride of barium precipitate 103·679, 103·679, and 103·662 of silver; mean 103·673. From this the equivalent of barium is deduced as 68·67.

During an investigation† regarding the equivalents of cerium, lanthanium, and didymium, in which I was obliged to make use of chloride of barium, I repeated some experiments analogous to those of M. Pelouze. As the mean result of a great number of experiments, I found that 100 of chloride of barium precipitate 103·772 of silver, which gives as the equivalent of barium, 68·57.

Subsequently, M. Salvetat‡ stated, that by ascertaining what was the loss of weight undergone by carbonate of baryta when decomposed by sulphuric acid, and calculating the equivalent of barium from this loss, he arrived exactly at the number 68. As carbonate of baryta can only be obtained by precipitation, it appears

* Comptes Rendus, vol. xx. p. 1051.

† Bibl. Univ. de Genève, June 1849; and Chem. Gaz. vol. vii. pp. 212, 329.

‡ Comptes Rendus, vol. xvii. p. 318.

to me that we can hardly be sufficiently certain of its purity to attach perfect confidence to this result.

Lastly, M. Struve* has converted chloride of barium into sulphate, and found that 100 of chloride produce 112·0912—112·0964, mean 112·0938 of sulphate, which would give for the equivalent of barium 67·86. It appears to me that this last process should be completely rejected, because it leads us to calculate a very high equivalent from the very small difference of weight which exists between the chloride and sulphate, so that the errors of the experiment are increased nearly ten times in the calculated result. Berzelius had already employed this method, and obtained 112·175 of sulphate for 100 of chloride, which would correspond with 67·17 for the equivalent of barium.

The first process followed by Berzelius, especially with the modification introduced into it by Pelouze, is so simple and capable of such precision, that it seems to me difficult to prefer any other. Moreover, the results obtained by three different experimenters agree very well with each other, so that the equivalent of barium would appear to me to be fixed by these three determinations with great certainty, if we were not able to raise a rather serious objection against the employment of this method—Is it possible to drive off all the water of the chloride of barium without causing it to lose chlorine?

I think there is but little ground for this objection. There is no doubt that it will not easily be admitted that Berzelius did not ascertain that this circumstance could not introduce any error into his experiment. Pelouze ascertained that the water driven off from chloride of barium at a red heat contains no trace of muriatic acid. I did not myself adopt this method until after ascertaining that when chloride of barium has been completely desiccated at a temperature little exceeding 212° F., it may be heated to redness, without undergoing the slightest diminution of weight. Such a diminution occurs to a very small extent when it is kept for a long time at a strong red heat, and it may then be proved that it has acquired a slight alkaline reaction, and that its solution is rendered turbid by carbonic acid. These observations would be sufficient, I think, to do away with all uncertainty. Nevertheless I acknowledge that no experiment has been made which gives a complete answer to the question above stated; and although it is impossible to compare a salt so neutral with the acids which retain water with great energy, such as boracic or stannic acid, it has not been established by a positive experiment that chloride of barium, when calcined at a temperature not sufficient to decompose it, does not retain some traces of water. I can only attribute to some such fear as this the uncertainty in which some chemists still are as to the true equivalent of barium, and the preference even given to the number 68 in a recent memoir by an illustrious philosopher, upon the equivalents of the simple bodies.

Convinced, for my own part, of the little reality of this objection,

* Liebig's Annalen, lxxx. p. 264.

I have thought that it would not be without interest to refute it by positive experiments; and it appeared to me that it would not be difficult to manage this without abandoning the principle of the method of M. Pelouze, by comparing the weight of the silver employed in the precipitation of the chloride of barium, not with that of this chloride itself, but with that of the sulphate of baryta which it is capable of producing. We thus completely avoid the necessity of driving off the water from the crystallized chloride, and consequently any error which might result from this operation. Sulphate of baryta is a salt undecomposable by heat, provided the introduction of reducing vapours be carefully avoided, so that the determination of its weight cannot induce any error.

Wishing, at the same time that I followed this new method, to take the same opportunity of checking my former determinations, I divided each observation into three experiments.

Crystallized chloride of barium undergoes no alteration in the air. I have seen crystals of this salt in an old collection of chemical products, contained for more than thirty years in an imperfectly closed wooden box, which had retained all their brilliancy and transparency. I have also assured myself that this salt is not sensitive to the hygrometric variations of the air. A certain quantity of this salt, reduced to a fine powder, placed in a very wide platinum capsule, kept for several days in my laboratory and weighed at different times, presented no variations of weight sensibly exceeding errors of weighing. Consequently when this salt has been reduced to a fine powder, and exposed for several days to the air, with frequent trituration and mixing in a mortar, it is easy to weigh, immediately after each other, three portions, and we have a right to count upon their absolute identity. These three portions, of which the first two were of 5 grms. each, and the third of 10 grms., and which I shall indicate by A, B, and C, were subjected to the following treatments:—

A. I dissolved 4·419 grms. of pure silver in pure nitric acid in a bottle with a ground stopper. The solution was diluted with water, and the first portion of the chloride of barium was dropped into it. The bottle was briskly agitated and kept in a warm place for an hour or two, so as to be certain that no fragments of chloride of barium remained, and then by means of a normal solution of silver, I determined the quantity of this metal necessary to complete the precipitation.

B. This portion was heated by degrees, and for a long time to dull redness in a platinum crucible. The crucible, afterwards furnished with a lid fitting very exactly, was set to cool under a bell-glass, dried by sulphuric acid, after which it was weighed rapidly. I then repeated the precipitation of the silver with this portion, precisely as in the preceding experiment. It is, as may be seen, the repetition of my old experiments.

C. This portion was weighed in a rather large platinum crucible. It was then heated to dull redness, and the loss of weight was determined. This operation, indeed, might not have been necessary, but

as it could have no inconvenience, I took the trouble to perform it, in order to make sure in this way, by comparison with the result of the preceding experiment, of the identity of two distinct portions of the same salt. After this I put into the crucible sufficient water to furnish a complete solution of the salt by the assistance of a gentle heat, and I then added, by means of a graduated burette, a determined volume of pure sulphuric acid, diluted with water, calculated so that there might be a slight excess of it, at the utmost a decigramme. The mixture was agitated for a long time, and heated on a sand-bath, so as never to reach ebullition.

The sulphuric acid employed for this operation had been previously purified and distilled by myself; but in order to avoid the impurities which may exist in such an acid when it has been kept for a long time in glass bottles, I had distilled a portion in a platinum retort before commencing these experiments.

Moreover, to assure myself that the employment of this acid did not introduce any foreign substance, and at the same time to prove the purity of the chloride of barium, I always proceeded in the following manner:—

After having agitated the mixture in the crucible long enough to be sure that the decomposition was complete, I let the sulphate of baryta settle as much as possible; then, when the supernatant fluid was perfectly clear, I removed it almost entirely by means of a very fine pipette, and let it run into a weighed platinum capsule. I replaced it by an equal quantity of water, agitated it, and allowed the precipitate to settle again. I decanted the clear liquid a second time into the capsule, then evaporated completely in the sand-bath both the liquid contained in the capsule and that remaining in the crucible; lastly, by calcination at a red heat, I drove off the small quantity of sulphuric acid which remained in these vessels.

In the three experiments made by me, the liquid evaporated in the platinum capsule left a grayish spot; the increase in the weight of the capsule was in each instance almost exactly a milligramme. Although this residue was undoubtedly composed in great part of sulphate of baryta, the insolubility of which in an acid liquid is not absolute, I did not consider that this weight should be added to that of the sulphate contained in the crucible, thinking that the loss thus produced might be compensated by a trace of fixed residue introduced by the sulphuric acid; but I think that this result excludes all danger of an error being produced by the use of this acid.

A useful precaution to be taken for the determination of the sulphate of baryta, consists in moistening it, after it has been weighed, with pure concentrated nitric acid, and allowing it to react for some time with the assistance of heat, after which it (the acid) is driven off by a gentle calcination, and weighed again. In one of my experiments I observed an evolution of reddish vapours and a slight alteration of weight after the second calcination, which proves that there had been a commencement of reduction of the sulphate of baryta. However, this inconvenience is not to be dreaded unless

the calcination be carried too far, which is not necessary to drive off the sulphuric acid completely. When this accident occurred, I took care to moisten the residue again with sulphuric acid, and repeated the calcination and weighing.

The series of operations just described was executed three times:—

1. With chloride of barium, which I had formerly purified by numerous crystallizations in water, and by precipitation by means of alcohol for my old experiments, and of which I still had an abundant supply.

2. With the same salt redissolved in water, and again precipitated by alcohol.

3. With the preceding salt again dissolved in cold water, and precipitated from this solution by a current of pure muriatic acid. I made this last experiment to meet an objection founded upon a fear which is no doubt much exaggerated. It might be asked whether chloride of barium which has been subjected to numerous alternate desiccations, solutions, and crystallizations, may not have undergone a partial decomposition, and whether it may not contain some traces of carbonate of baryta soluble in a concentrated solution of the chloride.

The salt precipitated in a fine powder by the muriatic acid was drained and pressed, and then spread in a large porcelain capsule, where it was left to dry at the ordinary temperature; it was then crushed in a mortar, and still left in the air until its weight presented no further variation.

The following are the results of these experiments:—

A. Crystallized chloride of barium, 5 grms.

	I.	II.	III.
Silver	4·4205	4·4195	4·4210

B. Crystallized chloride of barium, 5 grms.

Water	0·7395	0·7398	0·7400
Anhydrous chloride..	4·2605	4·2602	4·2600
Silver	4·4195	4·4200	4·4215

The comparison of these two series of experiments shows that no appreciable trace of chlorine is driven off at the temperature employed in the desiccation of the chloride of barium.

C. Crystallized chloride of barium, 10 grms.

Water	1·480	1·481	1·480
Anhydrous chloride..	8·520	8·519	8·520
Sulphate of baryta ..	9·543	9·544	9·542

If we double the weight of the silver employed in the experiments A, and compare it with the weight of sulphate of baryta obtained in the experiments C, we shall have for the equivalents

of sulphate of baryta..	116·57	116·61	116·55
of barium	68·57	68·61	68·55

or on the average 68·58 for the equivalent of barium. We arrive at the same result if, assuming as proved by the preceding experi-

ments, that chloride of barium heated to a dull red heat has become perfectly anhydrous and undergone no alteration, we calculate the equivalent of this chloride by the experiments B alone. They give, in fact, for the equivalent of barium 68·61, 68·59, and 68·55. I am thus brought back almost exactly to the same number which I obtained formerly (68·57).

Thus the equivalent of barium is not, any more than that of chlorine, a multiple by a simple number of the equivalent of hydrogen. But it would be sufficient to introduce a very slight modification into the experimental results, to render it an exact multiple of the half of that equivalent. All chemists who are disposed to admit the existence of simple relations between the equivalents of the simple bodies, will no doubt adopt the number 68·5. It is true that in all my experiments, as in those of M. Pelouze, the results have never reached so low a number, and it might be thought at the first glance that in so simple an experiment, in which one has scarcely to do anything but weigh the two bodies which are to react upon each other, it is difficult to admit an error which would rise to $\frac{1}{1000}$. But I must indicate that, besides its being impossible to answer for the absolute purity of the substances employed, there is in every chemical reaction by precipitation a cause of error which may slightly alter the results, so that one cannot count upon the strict exactness of the determinations made by this process, and they cannot be admitted as sufficiently near, unless it has been ascertained by experiment that this cause only acts within very restricted limits.

In my researches upon the equivalent of didymium*, I have shown that the equivalent of a sulphate cannot be exactly determined by the comparison of the weight of this sulphate and of the chloride of barium necessary for complete mutual precipitation, because the sulphate of baryta carries down and retains with it a very notable quantity of the soluble sulphate, even when the supernatant fluid contains an excess of chloride of barium.

The dread lest a similar cause might not render the preceding experiments inaccurate did not occur to me until after I had completed them, but I have made a new experiment which appears to me to prove sufficiently, that, although this cause of error actually exists, it acts so feebly that the definite result is but very slightly altered by it.

Five grammes of crystallized chloride of barium were heated to dull redness and left 4·258 of anhydrous chloride, which were put into a flask, containing the solution of 4·417 of silver. By the subsequent addition of a normal solution of silver, it was found that 2 milligrms. were necessary to complete the precipitation. A third milligramme was added after the lapse of 24 hours, without rendering the liquid turbid. After thoroughly agitating the whole, I collected the chloride of silver in a wide glass tube, drawn out at its extremity, of which the weight had been determined. It is very easy in this way to collect the chloride of silver with a rigorous exact-

* Chem. Gaz. vol. xii. p. 141.

ness, to wash it perfectly, and then to weigh it after desiccation, without its coming in contact with organic matters and without any possible loss.

The filtered liquid, as ought to be the case, was slightly rendered turbid by the addition of muriatic acid; but when I had passed over the chloride of silver a certain quantity of distilled water, there arrived a moment when this washing-water was, on the contrary, rendered turbid by nitrate of silver. Thus the chloride of silver precipitated retains a little chloride of barium in the midst of a liquid containing a slight excess of silver in solution, perhaps in consequence of the presence in this same liquid of a sufficient quantity of nitrate of baryta, since it subsequently yields this chloride to the pure water employed in washing.

Thus the term of the mutual precipitation of silver and a soluble chloride does not strictly correspond with the respective equivalents of these two bodies. But this cause of error is here confined within such narrow limits, that it only introduces into the final result a scarcely sensible modification. In fact, having united all the washing-waters as long as they continued to become turbid in the presence of salts of silver, I ascertained that the addition of a single milligramme of dissolved silver was sufficient to precipitate all the chlorine therefrom. Moreover, the weight of the chloride of silver collected in the pointed tube, after these washings and after desiccation, was 5·869, corresponding with 4·417 of silver. Now 4·419 of silver had been employed for the complete precipitation of the chloride of barium. Thus, far from being able to suppose that the chloride of silver after the washings still retains a portion of the soluble chloride, we see that there has been a slight, but still appreciable loss. This may be explained, either by the fact that no body, not even chloride of silver, can be regarded as absolutely insoluble, or by a possible impurity of the silver employed in these experiments, or by the loss which might have taken place during the solution of this metal. If it be due to these last causes, we commit a slight error in counting the whole of the silver employed in the experiment as having served in the precipitation of the chloride of barium.

This second cause of error acts in an opposite direction to that which results from the carrying down of a portion of the chloride of barium in the precipitate of chloride of silver; they appear also to be of about the same magnitude, so that we may hope that they nearly compensate one another*.

I regret that I did not subject all my preceding experiments to this mode of check, but I think I may conclude from the observation which I have just cited in detail, and from exactly similar phænomena which I have observed in the precipitation of the chlorides of strontium and lead, that it would not have changed anything in the conclusions which I have drawn from these experiments.

* The equivalent of barium calculated from the results of this last experiment alone, by the comparison of the weights of silver and chloride of barium, would be 68·56.

Perhaps it will be thought that the causes of error which I have just indicated, should lead us to renounce this method for the determination of chemical equivalents. I doubt, however, whether we could employ another which would present more guarantees of correctness. All may include some causes of error, but it is a very important point to be able to prove that their influence cannot give rise to any very sensible alteration in the results. Many methods which appear to us at the first glance to be excessively simple and correct, do not perhaps offer greater guarantees of accuracy. Can we assert, for example, that a metal reduced by hydrogen, or an oxide kept in a atmosphere of oxygen, does not afterwards retain by adhesion some traces of these gases, which it would be impossible to remove completely even in a perfect vacuum?

[To be continued.]

On the Action of Human Saliva upon Glucosides.

By G. Städeler.

As the ferment of saliva converts starch into sugar at the temperature of the body, it was not improbable that under suitable circumstances the glucosides would also undergo a decomposition by means of saliva. We know indeed that amygdaline resists its action, for it may be eaten without injurious effects, and passes, at least in part, without decomposition into the urine. This, however, is not the case with salicine; after this has been taken, the urine of man and animals contains saligenine with other products of decomposition.

The author therefore digested finely triturated salicine mixed with a quantity of water and fresh saliva, insufficient for its solution, for several hours at a temperature varying between 100° and 104° F., then evaporated it to dryness on the water-bath, and extracted the residue with æther.

On the evaporation of the æther, there remained an oleaginous, slightly yellowish liquid, which soon became converted into a soft crystalline mass. The crystals exhibited all the properties of saligenine; they dissolved readily in æther, alcohol, and hot water, and the very dilute aqueous solution immediately acquired a deep violet-blue colour on the addition of perchloride of iron. The residue extracted with æther also contained much sugar. The salicine had therefore undergone the same decomposition by the ferment of the saliva as by emulsine.

For the decomposition of 1 grm. salicine a quantity of saliva was employed, which could be collected within about a quarter of an hour; the minimum was thus no doubt exceeded; but even if this were not the case, it is far more convenient to collect a quantity of saliva for the preparation of saligenine, which is so interesting in many respects, than to prepare the expensive emulsine even only moderately pure.

Diastase, which also converts starch into sugar, does not agree in its action with the ferment of the saliva. When a cold-prepared

extract of germinating barley had been digested for hours at 104° F. with salicine, no trace of saligenine could be detected.

The author has not yet been able to institute any experiments with the ferment of the pancreatic juice. According to Schmidt's observations, it behaves like saliva with starch and amygdaline, and it is very probable that it also acts in the same way upon salicine. But even without taking this secretion into account, we may already assume that salicine, when swallowed, does not undergo decomposition in the organs, but in the stomach and small intestine, and that the saligenine produced is only sucked up and transferred to the urine.—*Journal für Prakt. Chemie*, lxxii. p. 250.

On the Occurrence of Creatine, and a simple Mode of preparing it. By G. Städeler.

The expression of chopped meat to obtain the fluid from which creatine is prepared by coagulation, treatment with baryta, &c., is a troublesome and tedious operation. The object is attained with much more ease, when the meat, minced or pounded with moderately coarse powdered glass, is mixed with 1 or 1½ vol. of alcohol, gently heated in the water-bath, and pressed. The extraction is so easily effected, that unless very large quantities of meat are to be operated on, a press is quite unnecessary. The alcohol is afterwards distilled away from the fluid obtained, the residue is precipitated with exactly the necessary quantity of neutral acetate of lead, the filtrate freed from lead by means of sulphuretted hydrogen, the sulphuret of lead separated by filtration, and the filtrate from this evaporated to a syrup. Even during cooling the creatine begins to crystallize. It is allowed to stand for some days, when the crystalline mass is spread upon white blotting-paper, which is laid upon a layer of damp brown paper, or a moistened glass plate, which readily imbibe the mother-liquors. The crystals are then collected, and recrystallized from hot water or from hot dilute alcohol.

In this way the author has very easily obtained an abundance of creatine from the muscles of the Ox, the Dog, the Pigeon, the Picked Dog-fish (*Spinax Acanthias*), and the River Lamprey (*Petromyzon fluviatilis*); it was obtained most abundantly from the flesh of the dog-fish, but in almost equal quantity from the pectoral muscles of the pigeon. Of the lamprey the author had only a single specimen at his disposal, and he was therefore obliged to content himself with ascertaining its presence by the crystalline form in the residue of evaporation of the extract made with absolute alcohol. The brain of the pigeon also contains no inconsiderable quantity of creatine; it occurred in smaller quantity in the brain of the dog, and urea was observed in company with it. This occurrence of creatine in the brain of the pigeon and the dog is the more interesting, as according to the observation of Dr. Müller of Erlangen, it is also present in the human brain, but absent in that of the ox. In the testes of the dog also crystals were repeatedly observed, which appeared to be creatine.—*Journal für Prakt. Chemie*, lxxii. p. 256

On the Composition of Phosphate of Soda and Lithia.

By C. RAMMELSBERG.

Twelve years ago the author described the phosphate of soda and lithia, and came to the conclusion that this compound is an isomorphous mixture of the terphosphates $(LiO, NaO)^3 + PO^5$, in which the proportion of the bases varies, so that the salt is not adapted for the determination of lithia. Upon this, as is well known, the author fouuded a method of separating lithia from the alkalies; the lithia is separated as chloride of lithium from the chlorides of potassium and sodium by means of a mixture of æther and alcohol.

Mayer has recently stated that the phosphate of soda and lithia has no existence. In his former experiments the author found that, besides lithia, 8—28 per cent. of soda may be contained in the double phosphate, and at the same time small quantities of carbonic acid were found.

The author now finds that carbonate of soda, when mixed in the cold with readily soluble, neutral phosphate of lithia, furnishes a crystalline precipitate, whilst phosphate of soda remains in solution. The precipitate not completely washed gave on analysis,—

		Oxygen.
CO^2	0·78	0·57
PO^5	61·37	34·40
LiO	32·52	17·90
NaO	1·48	0·37
HO	3·85	3·42

Deducting the small quantity of carbonic acid as carbonate of lithia and the soda as $2NaO + PO^5$, this precipitate is

$$2[(LiO)^2 + PO^5] + 3[(LiO)^3\,PO^5] + 2{\cdot}5Aq, \text{ or}$$
$$(LiO)^2\,PO^5 + (LiO)^3\,PO^5 + HO.$$

The phosphate of soda and lithia was prepared by the author from chloride of lithium, and phosphate and a little carbonate of soda, evaporated to complete dryness, and washed with cold water. When dried over sulphuric acid, the analysis of substance obtained in two operations gave,—

	I.	II.
CO^2	1·08	1·37
PO^5	54·39	55·72
LiO	23·25	26·89
NaO	20·36	14·89
HO	2·00	1·64

Both specimens were consequently $(LiO, NaO)^3\,PO^5$, and indeed

$$\text{No. I.} = 3(NaO)^3\,PO^5 + 7(LiO)^3\,PO^5$$
$$\text{No. II.} = 3(NaO)^3\,PO^5 + 4(LiO)^3\,PO^5.$$

Probably a solid isomorphous mixture with variable quantities of terphosphate of lithia was first formed during the evaporation. This mixture is perhaps $(NaO)^3\,PO^5 + (LiO)^3\,PO^5$. The author there-

fore declares the objections raised by Mayer against the existence of such salts to be destitute of foundation, and his method of decomposing the phosphates of lithia by baryta water, to be inapplicable, because then phosphoric acid remains in the fluid.—Poggendorff's *Annalen*, cii. p. 441.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

A Chemical Examination of the Commercial Varieties of Brown Sugar. *By* JOHN H. ALEXANDER *and* CAMPBELL MORFIT*.

THE impurities of crude sugars are incidental to the cane-juice and the process by which it is manufactured. They consist of water, insoluble or suspended matters, soluble organic matters, and uncrystallizable sugar. The latter is not only deficient in sweetening power, but conspires, with the water, organic matters, and chlorides of sodium and magnesium of the ash, to decompose the cane-sugar or valuable portion, and thus depreciate the real value of the commercial sugar.

Care was observed to secure fair average samples for the analyses, by having them selected through the agency of intelligent sugar-brokers of long experience. There was no free acid present in any one of them, as we determined by actual tests.

It having been found by preliminary qualitative examination that the same components were more or less common to all the samples, we arranged our plan of analysis so that it should in its progress detect and estimate the smallest quantity of either and all of them.

1. *Water.*—The moist condition of brown sugar is accidental, since it does not contain any water of crystallization. Its tendency to form hygroscopic compounds with the chlorides of sodium and magnesium gives to these salts, when present, the power of affecting materially the dryness of the sugar.

The amount of moisture was determined by weighing 25 grs. of the sugar upon a counterpoised watch-glass, and drying it *in vacuo* over sulphuric acid and chloride of calcium until it ceased to lose weight. The difference between the final and original weights expressed the amount of loss, which, being the contained water, was then calculated to per cent.

2. *Insoluble Matter.*—The totality of insoluble matter consisting of vegetable remains, sand, dirt, &c., was estimated by dissolving 100 grs. of the sugar in cold distilled water, filtering upon a counterpoised filter, washing repeatedly with cold water, then drying the filter *in vacuo*, and weighing. The weight represented the total amount of insoluble matter.

* Communicated by the Authors.

To separate the organic from the inorganic portion of this matter, the filter was burned to ash in a platinum crucible. The weight of the ash was taken as the per cent. of *inorganic* matter; and that which it had lost by ignition, as the *organic* portion.

3. *Albumen.*—The filtrate from the above was next concentrated by careful evaporation upon a sand-bath so as to coagulate the albumen, which was then separated upon a counterpoised filter. The filter having been thoroughly washed with cold water, was afterwards dried *in vacuo*, and weighed to obtain the per cent. of albumen.

4. *Caseine.*—A few drops of acetic acid were added to the remaining filtrate while hot, but without obtaining any perceptible reaction. Such would not have been the case had caseine been present; for though under the circumstances above noted it will not coagulate by heat alone, yet it readily separates upon the addition of an acid.

5. *Gum.*—After this treatment, the filtrate was evaporated nearly to syrup-consistence, and the gum precipitated from it by pouring in absolute alcohol. A counterpoised filter was used for the separation of the gum from the liquor, and after having been thoroughly washed with slightly diluted alcohol to remove all traces of sugar that may have gone down with the gum, it was then dried *in vacuo*, and weighed.

6. *Extractive.*—The colouring and undefined organic matters of the sugar, included under the term extractive matter, were estimated by treating the filtrate from the gum with a clear solution of subacetate of lead in bare excess, and immediately filtering upon a counterpoised filter, washing thoroughly with hot water, drying *in vacuo*, and weighing. As the extractive matter was alone carried down by the lead, it became necessary merely to ignite the precipitate and note the loss of weight in order to obtain the per cent. of extractive.

7. *Ash.*—The mineral constituents of the sugar were estimated by incinerating carefully 100 grs. in a platinum crucible so as to avoid vitrification of the ash. The latter was then weighed to ascertain its per cent., and subsequently put through a qualitative analysis for the purpose of determining its composition.

8. *Sugar.*—New quantities of the sugar were weighed for the estimation of the *cane-* and *uncrystallizable* sugars, and the proportion of each was ascertained directly by very careful manipulation and the processes of the books. It is proper to remark, however, that we have included under uncrystallizable or molasses-sugar, all the kinds present other than cane-sugar, such as chylariose and saccharo-glucose, both of which may owe their existence to a partial transmutation of the cane- or crystallizable sugar portion.

The following Table embraces all the varieties of brown sugar which were accessible at the time of analysis, but it is still wanting of several kinds, including the Sorghum sugar. Reliable average samples of these latter are now being procured, and a supplementary table of their composition will be given as soon as the analyses of them are completed.

Table of the Composition of Average Samples of the Commercial Varieties of Brown Sugar.

Number.....	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Name and source of specimen	Cuba, prime.	Cuba, fair.	Cuba, common.	Havana, prime.	Havana, fair.	Havana, common.	New Orleans, prime.	New Orleans, fair.	New Orleans, common.	Pernambuco, white.	Pernambuco, brown.	Porto Rico, prime.	Porto Rico, fair.	Porto Rico, common.	Trinidad, Cuba, common.
Cane-sugar	96·55	92·69	97·32	97·32	96·40	92·69	94·24	94·23	93·46	98·25	93·31	97·32	93·61	93·46	91·61
Water	1·70	2·70	·40	·20	1·20	1·00	1·60	1·30	2·20	·60	·30	·80	3·10	2·70	2·20
Uncrystallizable sugar	0·49	2·95	·38	·40	·65	1·66	·57	1·20	1·52	·23	·54	·12	·56	·94	2·35
Gum	·19	·32	·40	·15	·51	·32	·21	·14	·04	·23	·81	·16	·24	·56	·32
Albumen	·20	·18	·14	·14	·22	·96	·26	·16	·41	·14	·76	·52	·50	·52	·58
Extractive	·42	·94	·30	·87	·87	2·90	1·91	1·60	2·28	·47	2·46	·49	1·90	1·96	3·66
Ash*	·68	·57	·50	·50	·75	1·20	·78	·64	1·00	·24	1·24	·34	·40	1·15	·38
Suspended organic matter ..... (insoluble matter)	·26	·29	·10	·40	·20	...	·02	·05	·22	...	·24	·03	·22	·30	·39
Suspended inorganic matter ... (insoluble matter)	·22	·18	·09	·25	·20	·22	·14	·12	·16	·15	·92	·10	·12	·18	·09
Total.....	100·71	100·82	99·63	100·23	101·00	100·95	99·73	99·44	101·29	100·31	100·58	99·89	100·65	101·77	101·78

* Composition of the ash.

No. 1. Sulphuric, nitric, phosphoric, carbonic, and silicic acids; chlorine, potassa, soda, lime, magnesia, alumina.

No. 2. Phosphoric, carbonic, and silicic acids; chlorine, potassa, soda, lime, magnesia, and alumina.

No. 3. Sulphuric, phosphoric, carbonic, and silicic acids; chlorine, potassa, lime, magnesia, and alumina.

No. 4. Phosphoric, nitric, carbonic, and silicic acids; chlorine, potassa, soda, lime, magnesia, alumina.

No. 5. Phosphoric, carbonic, and silicic acids; chlorine, potassa, lime, magnesia, alumina, iron.

No. 6. Phosphoric, carbonic, and silicic acids; chlorine, potassa, lime, magnesia, iron, and alumina.

No. 7. Phosphoric, carbonic, and silicic acids; chlorine, potassa, soda, lime, magnesia, iron, and alumina.

No. 8. Phosphoric, carbonic, and silicic acids; chlorine, potassa, soda, lime, magnesia, iron, alumina.

No. 9. Phosphoric, carbonic, and silicic acids; chlorine, potassa, lime, magnesia, iron, alumina.

No. 10. Nitric, phosphoric, and silicic acids; chlorine, soda, lime, magnesia, iron, and alumina.

No. 11. Sulphuric, nitric, phosphoric, carbonic, and silicic acids; chlorine, potassa, lime, magnesia, iron, and alumina.

No. 12. Phosphoric, nitric, and silicic acids; soda, lime, magnesia, iron, and alumina.

No. 13. Phosphoric, nitric, carbonic, and silicic acids; chlorine, potassa, lime, magnesia, iron, and alumina.

No. 14. Phosphoric, carbonic, and silicic acids; chlorine, soda, lime, magnesia, iron, alumina.

No. 15. Phosphoric, carbonic, and silicic acids; chlorine, potassa, soda, lime, magnesia, iron, and alumina.

New Mode of Treating Speiss and Copper-nickel. *By* S. Clozz.

The crude material employed in the preparation of pure oxide of nickel is usually an arseniosulphuret of nickel, mixed with variable, and generally very small proportions of cobalt, iron, copper, antimony, and bismuth. The complete elimination of the arsenic contained in the native product called *nickeline* or *copper-nickel* (*Kupfer-nickel*), and in the manufactured product, known as *speiss*, is easily effected by converting it into sulphuret of arsenic which is soluble in alkaline sulphurets, or into arsenic acid, the compounds of which with alkalies dissolve readily in water.

The processes employed to separate the arsenic may also carry off the antimony where it exists, but the other metals remain mixed with the nickel in the form of sulphurets or oxides, and to separate them, the mixture must first be dissolved in an acid, the solution treated with sulphuretted hydrogen to precipitate the copper, lead, &c., and the liquid finally treated by various operations to remove the cobalt and iron.

The author has endeavoured to simplify the method by the action of sulphurous acid upon arsenic acid, which it converts into arsenious acid, and by the complete and rapid precipitation of the latter by sulphuretted hydrogen.

The mineral to be treated must be reduced to a fine powder and carefully washed to drive off the sulphur and the greater part of the arsenic. This may be done on the sole of a reverberatory furnace; in the laboratory, in a large roasting pot, heated in a blast-furnace, of which the draught may carry off all the the arsenious acid produced. The residue is dissolved by heat in concentrated muriatic acid; if the roasting has been imperfect, a portion of the material remains undissolved at the bottom of the flask, and is separated from the acid liquid by decantation. To the latter bisulphite of soda is then added in sufficient quantity to give rise to a great excess of sulphurous acid; and the whole is gently heated to boiling to complete the reduction of the arsenious acid, and drive off the excess of sulphurous acid.

A current of sulphuretted hydrogen gas is then passed into the liquid whilst still warm, to precipitate the arsenic with the copper, antimony, lead, and bismuth; the liquid saturated with sulphuretted hydrogen is left quiet for twelve hours, the precipitated sulphurets are separated by filtration, and the clear liquid containing, besides the nickel, a little cobalt and iron, is then evaporated to dryness.

The residue of the evaporation treated with water furnishes a clear and nearly neutral solution; it is treated with chlorine or a little chlorate of potash after the addition of a small quantity of muriatic acid; the iron and cobalt are thus converted into perchlorides; and carbonate of baryta or carbonate of lime is then added to precipitate these two metals in the form of sesquioxide: their separation is complete at the temperature of ebullition.

The liquid usually contains sufficient sulphuric acid, due to the oxidation of the sulphurous acid by the arsenic acid, to convert the carbonate of baryta or lime into insoluble sulphate; if this be not

the case, a certain quantity is added after the reaction so as only to have a single filtration to perform.

The filtered liquid only contains nickel; it is treated with a solution of an alkaline carbonate, and the precipitate formed, when washed and calcined, consists of chemically pure oxide of nickel, from which the metal may be easily extracted.

This process is equally applicable to the product resulting from the action of nitric or nitromuriatic acid upon speiss or German nickel, only in this case care must be taken to drive off all the nitric acid contained in the mixture, because the presence of nitrates in the acid liquid, after treatment by sulphurous acid, forms a kind of *aqua regia*, which, although very weak, is still strong enough to prevent the precipitation of the arsenic, antimony, &c. by sulphuretted hydrogen.

Before applying this method to the treatment of nickel ores, the author carefully tested the principal reaction involved in it. He mixed a solution of chloride of nickel containing 1 grm. of pure oxide with an aqueous arsenical solution, obtained by oxidizing 1 grm. of arsenious acid with nitric acid, evaporating to dryness, and treating the residue of arsenic acid with water. The liquid was heated to boiling with the addition of bisulphite of soda, and treated with sulphuretted hydrogen; the precipitated sulphuret of arsenic, collected on a filter, washed and dried at 230° F., weighed 1·264 grm., equivalent to the quantity of arsenious acid employed. The nickel was precipitated in the form of oxide; the quantity obtained was less by 5 milligrms. than that employed.—*Comptes Rendus*, January 4, 1858, p. 41.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 11, 1858. (Dr. Hooker, Vice-President, in the Chair.)

"Notes of Researches on the Poly-Ammonias." By Aug. W. Hofmann, Ph.D., F.R.S. &c.

Former investigations had led me to some general conclusions regarding the molecular constitution of the organic bases, which I have communicated to the Royal Society, and which have been published in the 'Philosophical Transactions' (1850, p. 93; 1851, p. 357). My experiments had proved that each equivalent of hydrogen in ammonium may be replaced by an equivalent of a mono-atomic electro-positive radical, such as methyle, ethyle, &c.;—a series of compound ammoniums being produced, the salts of which may be thus formulated:—

$$N\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right\}Cl. \quad N\left\{\begin{matrix}R'\\H\\H\\H\end{matrix}\right\}Cl. \quad N\left\{\begin{matrix}R'\\R'\\H\\H\end{matrix}\right\}Cl. \quad N\left\{\begin{matrix}R'\\R'\\R'\\H\end{matrix}\right\}Cl. \quad N\left\{\begin{matrix}R'\\R'\\R'\\R'\end{matrix}\right\}Cl.$$

R′ representing a mono-atomic electro-positive radical.

These successive substitutions were accomplished by the action of

ammonia upon the bromides and iodides of the alcohol-radicals, which since that time have become most valuable agents of substitution in the hands of chemists.

All the bases produced by this process being derived from 1 equiv. of ammonium, contain 1 equiv. of nitrogen; they differ in this respect essentially from the majority of the alkaloids extracted from plants, and more particularly so from those which, like quinine, morphine, strychnine, &c., specially claim our interest. By far the greater number of the vegetable alkaloids contain 2 equivs. of nitrogen. In some vegetable and animal bases we find even 3 and 4 equivs. of nitrogen. The molecular construction of these bodies is still obscure, but it is extremely probable that they are derived from 2, 3 or 4 ammonia equivs., in which the hydrogen is more or less replaced by poly-atomic molecules, and that the stability of such complicated structures essentially depends upon the substituting capacity of their replacing molecules.

It was long my intention to extend my researches to the poly-ammonium bases. But my attention has been specially called to the subject by the beautiful results obtained of late, especially in France, by the study of the poly-acid alcohols, by the experiments of M. Berthelot, and more particularly by the classical researches of M. Wurtz, which enable us to take a general view of this subject.

Taking as a point of departure the neutral compounds which are formed by the action of ammonia upon bibasic and tribasic acids, the *diamides* and *triamides*, derived respectively from 2 or 3 equivs. of ammonia, it became extremely probable that the action of ammonia upon poly-acid alcohols would give rise to poly-ammonium bases. In the conception of this analogy there appeared but little doubt that ammonia, under the influence of the bromides and iodides of bi-acid alcohols, would furnish a series of bi-ammonium bases, exactly as treatment of ammonia with the analogous compounds of mono-acid alcohols has given rise to the formation of the mon-ammonium bases above referred to. In other words, it was to be expected that a compound ether $R'' Br_2$ or $R'' I_2$ (R'' representing a bi-atomic electro-positive radical) would act upon two equivalents of ammonia, producing a series of salts expressed by the following formulæ:—

$$N_2\left\{\begin{matrix}R''\\H_2\\H_2\\H_2\end{matrix}\right\}Br_2. \quad N_2\left\{\begin{matrix}R''\\R''\\H_2\\H_2\end{matrix}\right\}Br_2. \quad N_2\left\{\begin{matrix}R''\\R''\\R''\\H_2\end{matrix}\right\}Br_2. \quad N_2\left\{\begin{matrix}R''\\R''\\R''\\R''\end{matrix}\right\}Br_2.$$

In endeavouring experimentally to verify this idea, it became necessary to examine what had hitherto been done in this direction. Science possesses already some very interesting observations on the ammonia derivatives of bi-acid alcohols. About five years ago, soon after the publication of my experiments upon the action of ammonia upon bromide and iodide of ethyle, M. Cloëz* obtained a series of bases, on submitting ammonia to the action of the brominated Dutch liquid ($C_4 H_4 Br_2$). Two of these bodies he described under the name of

* Instit. 1853, 213.

formylia and acetylia, whilst a third body subsequently obtained is designated by the term propylia*.

To these three bodies M. Cloëz attributes the following formulæ:—

Formylia..... C_2H_3N
Acetylia ..... C_4H_5N
Propylia ..... C_6H_7N.

At a later period M. Natanson has studied the action of ammonia on the chlorinated Dutch liquid ($C_4H_4Cl_2$). This reaction produces analogous results, but the number of bases is smaller, the chief product being a chloride, which contains a base either identical or isomeric with the acetylia of M. Cloëz.

When carefully considering the results obtained by M. Cloëz, it appeared to me probable that the bases which he describes, are in fact the di-ammonium compounds for which I was searching. The constitution assigned by M. Cloëz to his substances is not very probable. It is difficult to understand how the action of ammonia upon a compound like the Dutch liquid can produce simultaneously three bodies belonging to three different homologous families, the formyle-, acetyle-, and propyle-series. Our doubts are, however, increased if we examine into the physical characters of these bodies, especially if we consider their high boiling temperatures, and the differences between the boiling-points of the three bases:—

Formylia....	C_2H_3N	123°	} difference 47.
Acetylia	C_4H_5N	170°	
Propylia	C_6H_7N	210°	} difference 40.

Methylamine, C_2H_5N, which contains only 2 equivalents of hydrogen more than formylia, is at the common temperature a gas, and liquefies only considerably below the freezing-point of water. Again, the differences of the boiling-points of substances, related in the way that the formulæ of M. Cloëz suppose, do not often exceed 20°, and very rarely rise to 40° and 47°.

All these difficulties disappear by submitting the formulæ of M. Cloëz to a slight alteration, and by regarding formylia, acetylia and propylia as the di-ammonium bases of the same series, of the ethylene series. If we adopt this view, the three bodies are derived from 2 of ammonia, in which 2, 4 or 6 equivalents of hydrogen are replaced respectively by 1, 2 or 3 equivalents of the bi-atomic molecule ethylene; and the formylia, acetylia and propylia of M. Cloëz present themselves as monethylene-diamine, diethylene-diamine and triethylene-diamine.

I have endeavoured experimentally to solve this question. The analysis of acetylia, which is remarkable for the definite character of its salts, appeared to promise an answer to it.

When repeating the beautiful experiments of M. Cloëz, I had occasion to confirm all the indications given by this able chemist, regarding the formation of the bases derived from bibromide of ethylene. The analysis, however, furnished a discrepant result.

M. Cloëz represents formylia by the formula

$$C_2H_3N,$$

* Cahours, Leçons de Chimie Générale, t. ii. p. 654.

when the hydrochlorate becomes

$$C_2H_3N,\ HCl = C_2H_4NCl.$$

When considered as a di-ammonium compound, this salt has the composition

$$C_4H_8N_2,\ 2HCl = C_4H_{10}N_2Cl_2 = 2C_2H_5NCl.$$

The two formulæ only differ by one equivalent of hydrogen.

The analysis of a magnificently crystallized hydrochlorate has furnished me the following results:—

	Formula of M. Cloëz— C_2H_4NCl.		New formula— $C_4H_{10}N_2Cl_2$.		Mean of analysis.
Carbon	18·32	.....	18·04	.....	17·87
Hydrogen..	6·10	.....	7·51	.....	7·55
Chlorine ..	54·19	.....	53·38	.....	53·17

On preparing the free base by the action of hydrate of potassa upon the hydrochlorate, I was surprised to find that this body retains hydrogen and oxygen in the proportion in which they exist in water, which cannot be separated by prolonged contact with, or by repeated distillation over, anhydrous baryta.

The analysis of the free base has given the following result:—

	Formula of M. Cloëz— C_2H_4NO.		New formula— $C_4H_{10}N_2O_2$.		Analysis. Mean.
Carbon	31·58	.....	30·76	.....	30·67
Hydrogen..	10·52	.....	12·82	.....	12·97
Nitrogen ..	36·84	.....	35·90	.....	36·32

These numbers appear to me in favour of the formula which I propose for formylia; there remains but little doubt that acetylia and propylia are analogously constituted.

There remains yet to find the last term of the series, the tetrethylene-diammonium compound. Up to the present moment I have only established by experiment that the three lower bases are powerfully attacked by bibromide of ethylene, a non-volatile compound being produced possessing properties in every respect analogous to the character of tetramethyl- and tetrethylammonium.

If further experiments confirm the hypothesis which I have advanced, the action of ammonia on bibromide of ethylene would give rise to four compounds analogous to the bases which I have obtained by the action of bromide of ethyle.

Bromide of ethyl-ammonium.	$N\left\{\begin{matrix}C_4H_5\\H\\H\\H\end{matrix}\right\}Br.$	Bibromide of ethylene-diammonium.	$N_2\left\{\begin{matrix}(C_4H_4)''\\H_2\\H_2\\H_2\end{matrix}\right\}Br_2.$
Bromide of diethyl-ammonium.	$N\left\{\begin{matrix}C_4H_5\\C_4H_5\\H\\H\end{matrix}\right\}Br.$	Bibromide of diethylene-diammonium.	$N_2\left\{\begin{matrix}(C_4H_4)''\\(C_4H_4)''\\H_2\\H_2\end{matrix}\right\}Br_2.$
Bromide of triethyl-ammonium.	$N\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\H_5\end{matrix}\right\}Br.$	Bibromide of triethylene-diammonium.	$N_2\left\{\begin{matrix}(C_4H_4)''\\(C_4H_4)''\\(C_4H_4)''\\H\end{matrix}\right\}Br_2.$

Bromide of tetrethyl-ammonium, $N\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}Br.$ Bibromide of tetrethylene-di-ammonium. $N_2\left\{\begin{matrix}(C_4H_4)''\\(C_4H_4)''\\(C_4H_4)''\\(C_4H_4)''\end{matrix}\right\}Br_2.$

The conception of diammonium-compounds has suggested to me the idea to extend my observations also to the triacid-alcohols, and to submit ammonia to the action of the bodies

$$C_2H\,Br_3. \qquad C_4H_3Br_3. \qquad C_6H_5Br_3.$$

Analogy suggested the formation in this reaction of a series of triammonium-bases, the salt of which might be thus formulated:—

$$N_3\left\{\begin{matrix}R'''\\H_3\\H_3\end{matrix}\right\}Br_3. \quad N_3\left\{\begin{matrix}R'''\\R'''\\H_3\\H_3\end{matrix}\right\}Br_3. \quad N_3\left\{\begin{matrix}R'''\\R'''\\R'''\\H_3\end{matrix}\right\}Br_3. \quad N_3\left\{\begin{matrix}R'''\\R'''\\R'''\\R'''\end{matrix}\right\}Br_3.$$

I have not yet succeeded in realizing these compounds by treating under several conditions ammonia by the above chlorides and bromides of triacid-alcohols. The processes which I have as yet tried have led to other transformations. A different result is, however, obtained by replacing the ammonia in these processes by amidogen-bases. In this reaction, and especially with aniline and chloroform, a series of beautifully crystallized alkaloids is formed, the study of which engages at present my attention.

In conclusion, I may remark that several of the known basic compounds appear to belong to the triammonium-type.

The cyanethine of Kolbe and Frankland may be viewed as such a compound—

$$C_{18}H_{15}N_3=\left\{\begin{matrix}(C_6H_5)'''\\(C_6H_5)'''\\(C_6H_5)'''\end{matrix}\right\}N_3.$$

This substance appears to me to be derived from 3 equivs. of ammonia, in which 3 equivs. of hydrogen are replaced by 3 equivs. of the tri-atomic radical which chemists assume in glycerine-alcohol.

March 18, 1858. (The Lord Wrottesley, President, in the Chair.)

"On the Constitution of the Essential Oil of Rue." By C. Greville Williams, Esq., Lecturer on Chemistry in the Normal College, Swansea.

The essential oil of rue and its products of decomposition have been examined by several chemists. Will analysed it many years ago, and deduced the formula $C^{28}H^{28}O^3$ as the result of his analyses. The principal investigation of it was made by Gerhardt, who regarded it as the aldehyde of capric acid. The production of capric acid from it by the action of nitric acid, as observed by Gerhardt and also by Cahours, has been considered as corroborative of the 20 carbon formula. It is evident, however, that the formation of capric acid merely indicates the aldehyde to contain *not less* than 20 equivalents of carbon.

Some experiments made with a view to the production of certain new derivatives of capric aldehyde, led the author to believe the ideas

generally entertained regarding the formula of the oil to be erroneous. Before continuing his experiments, he has therefore reinvestigated the nature of the oil itself.

In order to obtain the aldehyde in a state of purity, advantage was taken of the tendency of the aldehydes to combine with the alkaline bisulphites. The oil obtained from the ammoniacal bisulphite of the aldehyde was carefully analysed. The mean of eight very coincident analyses gave,—

	Mean.		Calculation.	
Carbon.....	77·71	C^{22}	132	77·65
Hydrogen ..	13·07	H^{22}	22	12·94
Oxygen	9·22	O^{2}	16	9·41
	100·00		170	100·00

The mean of two determinations of the density of the vapour * gave,—

Experiment (mean).	Theory $C^{22}H^{22}O^{2}$ = 4 vols.
5·870	5·874

The aldehyde, purified as above, was again converted into the ammoniacal bisulphite, from which the oil was a second time obtained. It gave on analysis,—

Carbon.....	77·67
Hydrogen	12·93
Oxygen.....	9·40
	100·00

It is plain, therefore, that oil of rue contains an aldehyde of the formula $C^{22}H^{22}O^{2}$. Recent researches having demonstrated that no acid of the series $C^{n}H^{n}O^{4}$ with 22 equivalents of carbon has yet been isolated, and no other derivative with a 22 carbon formula being known, the author has given the name *enodyle* to the radical homologous with acetyle contained in this substance.

Enodic aldehyde is a colourless fluid of a fruity odour, quite different to that of the rue plant. Its density is 0·8497 at 15°. Agitation will cause it to solidify at 7° into a snow-white mass resembling camphor. Its boiling-point is 213°.

Rue oil yields a small portion of fluid boiling at 232°, containing the aldehyde of lauric acid. It was not obtained absolutely free from the first fluid. It contained:—

	Experiment.		Calculation.	
Carbon	78·1	C^{24}	144	78·26
Hydrogen	12·9	H^{24}	24	13·04
Oxygen	9·0	O^{2}	16	8·70
	100·0		184	100·00

The oils accompanying the aldehydes, but which refuse to combine with the alkaline bisulphites, are of the terebinthinate class. The more volatile are composed chiefly of an isomer of oil of turpentine; the less volatile are hydrates apparently homologous with an isomer of borneol.

* In order to prevent oxidation of the oil, the balloons were filled with hydrogen previous to immersion in the bath.

THE CHEMICAL GAZETTE.

No. CCCLXXIII.—May 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Amount of Platinum in the Platinum Residues.

By A. MUCKLÉ *and* F. WÖHLER.

A CONSIDERABLE quantity of black crystalline perchloride of iridium and ammonium, prepared according to the well-known process from ordinary platinum residues, was, in order to convert it into double cyanide, finely triturated and poured over with a solution of cyanide of potassium. The salt exhibited a remarkable change of colour, it became pale yellowish-brown, the fluid at the same time acquiring an odour of hydrocyanic acid or cyanide of ammonium. When the colour, after a gentle digestion, had become perfectly uniform, and the salt underwent no further change, the fluid was poured away, the salt washed several times with cold water, and then treated with hot water, in which it dissolved completely and with a yellow colour. On cooling, it again separated, and indeed crystallized in small, very shining, regular octahedra of a yellow colour. The more slowly the cooling took place, the larger were the crystals, and the deeper their yellow colour. When heated to redness, they yielded muriate of ammonia and a mixture of chloride of potassium, and a gray metal. This metal, most unexpectedly, proved to be *platinum*. It was readily dissolved by nitromuriatic acid with the colour peculiar to it, and from this solution pure yellow salt was thrown down by muriate of ammonia and chloride of potassium. The analysis of this salt, which was easily effected, showed that it is a mixed salt composed of potassio- and ammonio-chloride of platinum, in accordance with the formula $PtCl^2+\left.\begin{matrix}KCl\\NH^4\end{matrix}\right\}Cl$. There were found in 100 parts,—

Pt	41·85	$PtCl^2$	71·95
Cl	45·36	KCl	17·93
K	9·41	NH^4Cl	10·15
NH^4	3·41		

This salt was on this occasion obtained in such large quantity from the black iridium salt, which was apparently quite free from platinum, that we were almost led to suppose that there was a conversion of iridium into platinum. But it soon appeared that we had to do only with a separation of the two metals; for the fluid poured away from the platinum salt actually contained an almost equal quantity of iridium, in the form of double sesquichloride. Moreover, we could not procure a trace of platinum in this way from perchloride of ammonium and iridium, prepared from perfectly pure sesquichloride of ammonium and iridium, for which we are indebted to the kindness of Professor Claus. On the other hand, a considerable amount of platinum could be obtained from all the samples of black chloride of ammonium and iridium, which had been prepared from various kinds of residues, partly from St. Petersburg and partly from Paris, a proof that these residues still contain platinum, which cannot be extracted by nitromuriatic acid. We estimate its quantity to be sufficiently large to deserve attention in a practical point of view.

To extract the iridium by means of cyanide of potassium from perchloride of iridium and ammonium containing platinum, some care is necessary, otherwise much platinum salt is also dissolved, and finally converted into double protocyanide. An excess of solution of cyanide of potassium must be avoided as much as possible, and this must be gradually mixed with the finely powdered salt, and gently digested with it only until it has uniformly changed its colour, when it is treated as above described. The process is evidently not adapted to a quantitative separation.

The great influence of perchloride of ammonium and iridium upon the colour of the chloride of ammonium and platinum crystallizing together with it, was shown in some experiments, in which we allowed definite quantities of pure chloride of ammonium and platinum to crystallize with pure perchloride of ammonium and iridium, purified by the method of Claus:—

1 part of iridium salt and 2 parts of platinum salt give perfectly black, opake crystals.

1 part of iridium salt and 3 parts of platinum salt give brownish-black crystals, transmitting dark red light.

1 part of iridium salt and 5 parts of platinum salt give dark blood-red crystals.

1 part of iridium salt and 7 parts of platinum salt give pale red crystals.

1 part of iridium salt and 9 parts of platinum salt give dark red crystals.

The depth of colour, however, as is seen in the last example, in which larger crystals were formed than in 1 : 7 is very comparative, and is greatly modified by the unequal size of the individual crystals. At any rate it is evident that crystallized perchloride of iridium and ammonium, such as we possess in unusually large, black octahedra, may contain more than the half its weight of chloride of platinum and ammonium, without this being perceptible in the colour.—Liebig's *Annalen*, December 1857, p. 368.

On Compounds of Molybdenum with Nitrogen. *By* E. URLAUB.

The author describes the following compounds:—

Molybdonitretamide, $4MoN + Mo(NH^2)$.—It is produced when perfectly dry ammonia is passed over perchloride of molybdenum, which is formed by heating the metal in dry chlorine free from air. The action of the ammonia takes place at ordinary temperatures; the mass becomes heated and fuses, and muriate of ammonia is volatilized. It is afterwards heated, when a black, vesicular, cindery mass is obtained, which shines at the point where it has been closely applied to the wall of the glass. This is pounded, freed from muriate of ammonia by rapid washing with water, and dried over sulphuric acid.

The black powder, when heated in the air, evolves ammonia, and then suddenly becomes incandescent throughout with volatilization of molybdic acid; when a stronger heat is applied, all the molybdenum is evolved as molybdic acid. When treated with hypochlorite of soda, the reaction of nitrogen is obtained; with hydrate of potash this product evolves ammonia. Analysis:—

Mo	76·25	5	76·15
N	23·07	2	23·19
H	0·68	2	0·66

This compound is not easily obtained.

Bimolybdonitretamide, $4(Mo^6N) + MoNH^2$, is formed when perchloride of molybdenum is treated with gaseous ammonia, and finally exposed to a temperature at which the glass tube becomes slightly red-hot; at the same time a small quantity of molybdamide is produced. It resembles the preceding body in its appearance and properties. Analysis:—

Mo	85·37	9	85·18
N	14·28	5	14·41
H	0·35	2	0·41

Trimolybdonitride, Mo^3N, is obtained by a stronger ignition of the perchloride in a current of dry ammonia. Resembles the preceding, but is more gray. Analysis:—

Mo	90·72	3	90·78
N	9·28	1	9·22

These various nitrides are reduced at a white heat in the current of ammonia.

It is remarkable that the hydrogen in these compounds still persists at a high temperature, and even at a still higher traces of it may be met with in them.

Protochloride of molybdenum, treated with gaseous ammonia, furnishes the same nitrides. In these experiments the author has discovered a compound analogous to the platinum bases.

At ordinary temperatures gaseous ammonia acts upon perchloride of molybdenum; heat is evolved, and thereby some muriate of

ammonia is volatilized. The reaction takes place in accordance with the following equation:—

$$10NH^3+3Mo\,Cl^2=3N\left\{\begin{matrix}Mo\\H\\H\\NH^4\end{matrix}\right\}+3NH^4\,Cl+N.$$

The molybdenum compound, $N(Mo\,H^2, NH^4)\,Cl$, is decomposed by the heat evolved, as has already been observed, into muriate of ammonia and $N(Mo\,H^2)$, and the latter is then partially decomposed into hydrogen and Mo N.

Molybdamide cannot be entirely converted into this compound, as at a high temperature a decomposition into nitrogen and $Mo^2\,N$ occurs. The $Mo^2\,N$ is not obtained free from the compound $Mo\,NH^2$; when the temperature is raised, it is gradually decomposed into that nitride, but at the same time originates a decomposition of the $Mo^2\,N$ into $Mo^3\,N$. At a strong red heat, the nitride is reduced to the metallic state by the gaseous ammonia.

The author endeavoured to produce the various nitrides by the action of ammonia upon molybdic acid. He first of all gently heated molybdic acid in gaseous ammonia; in other cases he applied a stronger heat, and then obtained mixtures of the compounds mentioned below. Lastly, at a white heat, he obtained metallic molybdenum. The products which were obtained by such processes were mixtures, of the following of which the author describes the preparation and analyses.

With a gentle heat pseudomorphs of the following composition were produced:—

$$Mo\,NH^2, Mo\,O^2+4Mo\,O^3.$$

With the glass tube at a slight red heat, products of the composition—

$$Mo\,NH^2, 3Mo\,O^2 \text{ and } Mo\,O^3.$$

When the temperature was raised still higher, the author obtained products of the composition—

$$Mo\,N, 2Mo\,NH^2, 8Mo\,O^3.$$

When molybdic acid was heated in ammonia in a glass tube difficult of fusion and gradually heated to redness, the author obtained a product—

$$2Mo^2\,N, Mo\,NH^2+6Mo\,O^2.$$

When the same acid, placed in a porcelain tray, was heated in the current of ammonia in a porcelain tube which was brought to slight redness, he obtained the product—

$$2Mo^3\,N, 2Mo^2\,N+3Mo\,O^2.$$

When the temperature was still further raised, pseudomophs were obtained which had a gray appearance, and scarcely contained traces of hydrogen. The analysis gave—

$$Mo=87{\cdot}39\quad O=4{\cdot}15\quad N=8{\cdot}46.$$

The author also found that the oxide of molybdenum, prepared according to Berzelius' directions, by the ignition of molybdate of soda with muriate of ammonia, contains nitrogen and small quantities of hydrogen.—Poggendorff's *Annalen*, ci. p. 605.

On the Chemical Equivalents of Barium, Strontium, and Lead. *By* C. MARIGNAC.

[Concluded from page 148.]

Equivalent of Strontium.

Berzelius states that, according to Stromeyer, 100 parts of anhydrous chloride of strontium produce 181·25 of chloride of silver. This result, calculated with the equivalents 108 for silver and 35·5 for chlorine, gives 43·67 for the equivalent of strontium.

Pelouze, applying to the determination of this equivalent the same method which he had employed for barium, found that 100 of anhydrous chloride of strontium require for their complete precipitation 136·081—136·108 of silver, from which the numbers 43·864 and 43·848 result for the equivalent of strontium:—mean 43·85.

Salvetat states that he arrived exactly at the number 44 by the conversion of the carbonate into sulphate. This method does not appear to me to be of a nature to give perfectly certain results.

To check the preceding determinations, I employed the same method as for chloride of barium. The experiments were conducted in exactly the same manner, so that I have but few details to add upon their course.

The essential point was to obtain perfectly pure chloride of strontium. With this view, I took the pure chloride of the manufacturing chemists, dried it at a red heat, and dissolved it again in water; it scarcely left any trace of insoluble residue. I boiled its solution for a long time with a small quantity of pure sulphuric acid, taken from an acid of known strength. The precipitate, collected and calcined, presented a weight corresponding almost exactly with that indicated by calculation for sulphate of strontia. It therefore contained no sulphate of baryta, or very little; in any case, considering the difference of the solubility of the sulphates of these two bases, I was sure, after this, that I had no baryta in the solution.

To get rid of lime, I precipitated the chloride of strontium from its aqueous solution, by causing the latter to absorb muriatic acid gas. The crystallized precipitate was washed upon a funnel with pure muriatic acid, then pressed and dried in the air. This process appeared to me well adapted to eliminate chloride of calcium, which dissolves very readily in concentrated muriatic acid, whilst chloride of strontium is but slightly soluble therein.

Moreover, it is easy in these experiments to prove the purity of the salt employed by the solubility of the sulphate of strontia. When I evaporated to dryness the clear liquid separated by decan-

tation from the sulphate of strontia (experiment C), there always remained a very considerable residue, about 0·070 grm. for 50 cub. cent. of decanted liquid. This considerable weight, which would correspond with a solubility of about $\frac{1}{700}$, might lead us to suppose the presence of sulphates more soluble than that of strontia, but it is easy to ascertain that its excess is due, either to the nascent state of the sulphate (which, as is well known, is only completely precipitated after a considerable time), or to the presence of a great excess of muriatic acid. In fact, in determining the solubility of this residue after calcination, I always obtained numbers included between $\frac{1}{6000}$ and $\frac{1}{6500}$, which entirely excludes the possibility of the presence of other bases besides strontia.

Although chloride of strontium is far from being as insensible as that of barium to the variations of atmospheric humidity, I have nevertheless remarked that the changes of weight which it may undergo during the period of three weighings are quite insensible. Perhaps this would not be the case in all seasons, but these experiments were made during a very dry and cold January, so that this chloride kept perfectly in the state of a dry powder.

Four series of experiments were made:—

1. Upon the chloride purified as I have just described, and dried spontaneously in the air after its precipitation by muriatic acid. I shall not relate the results of this first series, having ascertained that the salt had retained a slight acid reaction, and that its purity was not yet absolute, the solubility of its sulphate having been found to be $\frac{1}{4500}$.

2. The preceding chloride was dissolved again in water, precipitated by strong alcohol, and then washed on a funnel with alcohol.

3. The preceding chloride was strongly desiccated, dissolved again in water, treated with carbonic acid and boiled, which did not cause any precipitate in it; then, after cooling, it was again precipitated by alcohol.

4. The last, after a new crystallization in water.

I took care, in all these experiments, to collect the chloride of silver arising from the precipitation; I always saw the repetition of the facts which I have indicated for chloride of barium. The chloride of silver also retains a trace of chloride of strontium, even when it is precipitated in the presence of an excess of silver salt; this chloride is afterwards removed from it by washing with pure water, but its total quantity is equivalent at the utmost to a milligramme of silver. The weight of the chloride of silver was always less by 2 or 3 milligrms., than that which would be indicated by calculation from the quantity of silver employed in the precipitation. This difference was so constant, that I have thought it useless to cite here the weights found for this chloride of silver.

The following are the results obtained in the last three series of experiments made upon perfectly pure salts.

A, 5 grms. of crystallized chloride of strontium:—

Silver	4·0515	4·0495	4·0505

B. 5 grms. of crystallized chloride:—

Water	2·0278	2·0284	2·0283
Anhydrous chloride	2·9722	2·9716	2·9717
Silver	4·0490	4·0500	4·0490

C. 10 grms. of crystallized chloride:—

Anhydrous chloride..	5·942	5·941	5·942
Sulphate of strontia..	6·887	6·8855	6·884

A comparison of the experiments A and B shows that chloride of strontium, dried at a gentle red heat, did not undergo any sensible loss of chlorine, the difference found being due to errors of observation. We may consequently calculate the equivalent of strontium by means of the experiments B alone; by comparing the weights of silver and chloride of strontium, we thus find—43·77, 43·74, and 43·76.

On the other hand, if, in the experiments A and C, we compare the weights of silver and sulphate of strontia so as to get rid of all uncertainty arising from the action which the heat may exercise upon the crystallized chloride of strontium, we find the numbers 43·79, 43·82, and 43·77. The mean of the former is 43·76, that of the latter 43·79. We may therefore assume the number 43·77 for the equivalent of strontium; it is precisely the mean between that of Berzelius and that of Pelouze. We may equally well take 43·75; it is impossible to answer for such differences.

But I regard this result as important, because it appears to me impossible to suppose errors in my experiments capable of carrying the true equivalent of strontium to 43·5 or to 44. If, therefore, we wish to assume the existence of simple relations between equivalents, we are forced to lower still further the unit which may serve as their common measure. After having been obliged to have recourse to half the equivalent of hydrogen to enable us to express in simple numbers the equivalent of chlorine, and perhaps those of copper, barium, and lead, we must again halve this unit for strontium.

It is true that, in fact, if the common relation is no longer the actual equivalent of hydrogen, but a fraction of this equivalent, there is no reason why this fraction should be $\frac{1}{2}$ rather than $\frac{1}{3}$, or any other much smaller fraction, $\frac{1}{100}$ for example. This is as much as to say that this question of the existence of a unit, of which the weights of all chemical equivalents would be simple multiples, will always be incapable of solution by experiment.

Equivalent of Lead.

The equivalent of lead was determined by Berzelius by the reduction of oxide of lead by hydrogen. He found that 100 parts of lead combine with 7·725 of oxygen, which leads to the number 103·56 for the equivalent of this metal.

I knowof no other determination of this equivalent. The simplicity of the method followed by Berzelius, and the well-known accuracy of that philosopher, appear to me scarcely to justify the

elevation of this equivalent to the number 104, as has been done sometimes to bring it amongst the multiples of hydrogen.

Without supposing that the method which I have described for barium could, in this case, furnish results more certain than those which may be arrived at by direct experiments upon the oxidation of lead or on the reduction of its oxide, I have thought that it would nevertheless be interesting to try its application to lead also. But I was compelled to give up following exactly the same course, by the impossibility which I met with of decomposing chloride of lead entirely by sulphuric acid. After having heated it, then dried it, and calcined it with an excess of this acid, it was still partly intact. I have no doubt that this might be done by employing vessels large enough to dissolve the chloride entirely in water, but then the experiment would lose much of its simplicity and exactitude.

Moreover, chloride of lead, being anhydrous, only retains a trace of interposed water, which is very easily driven off when this salt, reduced to a fine powder, is heated to about 392° F. After this it is no longer at all hygrometric, and no decomposition is to be feared. I think that we may count upon the exactitude of the result obtained by determining the weight of silver required to precipitate exactly a given weight of chloride of lead dried at about 392° F. The facility with which this salt may be obtained in a state of purity by two or three crystallizations in boiling water, still further simplifies this method.

The precipitation of silver by chloride of lead requires some preliminary precautions. After having dissolved the silver, 3·880 grms. for 5 grms. of chloride of lead, the latter salt may be introduced into this solution, either in powder or in the solution formed separately in water by boiling. If the salt be employed in the solid state, it reacts only with considerable slowness upon the solution of silver in consequence of its slight solubility. It must therefore be left to act for several hours in operating with the aid of heat, and for one or two days, if the bottle be left at the ordinary temperature, before trying the addition of the standard solution of silver which is to complete the precipitation. In this case, the operation lasting a considerable time, it is indispensable that the bottle should be perfectly preserved from the influence of light; this precaution, moreover, must never be neglected when it is intended to make an exact determination of chlorine. Under the influence of light, in fact, the chloride of silver is decomposed, producing an evolution of chlorine which induces the precipitation of a fresh quantity of silver. I have proved that when an experiment of this nature is made, the chloride being left exposed even to diffused light, a milligramme of silver may be introduced into the fluid every day, always producing a fresh precipitate, even when the precipitation of the chlorine was complete on the first day. When the light is bright, small bubbles of gas are seen raising the particles of chloride of silver; it is probable that these are oxygen produced by a decomposition of water by the chlorine set free.

If the silver has been precipitated by means of the boiling solution of chloride of lead, and generally whenever the liquid in which the precipitation is effected has been brought to a high temperature, it is necessary to let it cool completely before trying whether the addition of the standard solution of silver will render it turbid. In the first two experiments, which I made before recognizing the importance of this precaution, I found it impossible to fix within six or eight milligrammes of silver the termination of the precipitation. In a perfectly cold liquid, on the contrary, this termination presents no uncertainty.

It was natural to suppose that this difficulty must be due to the solubility of chloride of silver in a hot solution of nitrate of lead. The correctness of this explanation is easily established. Having dissolved 5 grms. of nitrate of lead in cold water, and added to this solution some nitric acid and a few drops of muriatic acid, the addition of a milligramme of silver produced a very perceptible turbidity, which, however, disappeared completely as soon as the liquid was heated. When it is brought to ebullition, 8 or 9 milligrms. of silver may be added to it before the appearance of a precipitate; but in all cases the latter appears when the solution cools.

In these experiments, as in those relating to strontium, I collected, washed and weighed the precipitate of chloride of silver, and observed the same facts that I have already indicated. It did not appear to me to retain a sensibly larger quantity of chloride of lead than that of the chlorides of barium and strontium. The weight of the chloride of silver was also less by 2 or 3 milligrms. than that which ought to have been furnished by the weight of silver precipitated.

The following are the results obtained, omitting two first experiments in which the completion of the precipitation remained uncertain:—

Chloride of lead, dried at about 392° F. ..	4·9975	4·9980	5	5
Silver	3·8810	3·8835	3·8835	3·8860
Equivalent of lead ..	103·57	103·49	103·55	103·46

The mean of these results would be 103·52, and consequently confirms the equivalent adopted by Berzelius. We may, however, assume 103·5, without exceeding the limits of errors of observation. —*Bibl. Univ. de Genève*, March 1858, p. 209.

On two new Metals in the Swedish Magnetic Iron Ore.
By Professor ULLGREN.

I have recently received a magnetic iron ore from Westerby, near Askersund in Sweden, sent for analysis, with the statement that a small addition of this ore in the smelting of good ores, caused a high degree of deterioration of the iron obtained. In the analysis which I made of this ore, I believe I have discovered two metals, one of an electro-negative, the other of an electro-positive nature, and with

properties which justify the assumption that they have not yet been made known.

The electro-negative metal has the following properties:—it is thrown down with a brown colour by sulphuretted hydrogen from an acid solution, and the precipitate is soluble with a brown colour in ammonia and sulphuret of ammonium. Its solution in nitro-muriatic acid, when slowly evaporated, deposits a solid body of a brownish-yellow colour. Before the blowpipe this gives colourless globules with salt of phosphorus, and furnishes no metal with soda upon charcoal.

The properties of the electro-positive metal are as follow:—From a solution of iron, mixed with a sufficient quantity of acetate of soda, it is thrown down by sulphuretted hydrogen, together with iron and a small amount of zinc which is contained in the ore. After the precipitate has been partially dried upon the filter, iron and zinc may be removed by dilute muriatic acid, and afterwards nitric acid. The residue, calcined with access of air, and afterwards fused with carbonate of soda, yields a grayish-yellow substance, which when calcined in hydrogen gas furnishes a black powder, which burns in the air to a grayish-yellow body. The black powder obtained by reduction with hydrogen gas, is dissolved with extreme difficulty by nitric acid, but more readily by nitromuriatic acid; in this solution alkalies form a yellowish-brown, flocculent precipitate, ferrocyanide of potassium a blue or green one. Before the blow-pipe it gives a colourless globule with salt of phosphorus; this becomes opalescent in the inner flame, and when a large quantity is present, gray. It is not in the least attracted by the magnet.—Liebig's *Annalen*, December 1857, p. 336.

On Eugenic Acid. *By* C. Greville Williams*.

The composition of the acid portion of oil of cloves has engaged the attention of several chemists. It has been examined by Dumas†, Ettling‡, Böckmann§, Stenhouse‖, and more recently by Calvi¶. The following are the results of their analyses:—

	Dumas.			Ettling.	Böckmann.
Carbon	68·95	68·96	69·11	71·63	71·7
Hydrogen	7·88	7·23	7·10	7·44	7·4
Oxygen	23·17	23·81	23·79	20·93	20·9

	Stenhouse.		Calvi.				
Carbon	72·24	72·02	72·7	72·4	72·7	72·7	72·6
Hydrogen	7·21	7·41	7·0	7·0	7·0	7·3	7·3
Oxygen	20·55	20·57	20·3	20·6	20·3	20·0	20·1

The formula deduced by Dumas was $C^{40}H^{24}O^{10}$; that of Ettling,

* Communicated by the Author.
† Ann. der Chem. u. Pharm., ix. 65; xxvii. 151.
‡ *Ibid.* ix. 68.
§ *Ibid.* xxvii. 155.
‖ *Ibid.* xcv. 103.
¶ Traité de Chimie Organique, vol. iv. p. 1037.

adopted also by Stenhouse, $C^{48}H^{30}O^{10}$. Neither the vapour-density as determined by Dumas, nor the composition of the baryta-salt as analysed by Ettling, agree with either of those expressions, which are evidently inadmissible for an essential oil. Gerhardt has long suggested $C^{20}H^{12}O^{4}$ as being a more probable formula, and agreeing also with Ettling's estimation of the baryta in the eugenate. M. Calvi's analyses, although nearer the number required for the latter formula, cannot be considered as settling the question, his determinations of the carbon and hydrogen being too low. The following are the per-centages corresponding to the above formulæ:—

	$C^{40}H^{24}O^{10}$	$C^{48}H^{30}O^{10}$	$C^{20}H^{12}O^{4}$
Carbon	69·77	72·36	73·17
Hydrogen	6·98	7·54	7·32
Oxygen	23·25	20·10	19·51

The vapour-density, as determined by Dumas, was 6·4. The formula $C^{48}H^{30}O^{10}$ requires 13·77, and $C^{40}H^{24}O^{10}$ 11·9 for 4 volumes. Gerhardt's formula requires 5·67. Ettling found 32·8 per cent. of baryta in the eugenate; the numbers corresponding to the formulæ are as follows:—

$C^{48}H^{28}O^{8}, 2BaO.$	$C^{40}H^{22}O^{8}, 2BaO.$	$C^{20}H^{11}O^{8}, BaO.$
28·70	31·94	33·04

I have long intended to make experiments with a view to obtain certain derivatives of eugenic acid, but before undertaking them I wished to assure myself of its true formula. The results have been lying by while working on other subjects, but the appearance of the paper of M. Cahours*, in which he investigates the action of the chlorides of certain oxidized radicals upon eugenic acid, renders it necessary to publish them in their present state.

Good oil of cloves was treated with moderately strong solution of potash, by which it was chiefly dissolved, about a tenth being insoluble. The alkaline solution, after separation with a tap-funnel and boiling for a short time, to remove the last traces of the hydrocarbon, was treated, when cold, with an acid in excess, on which the eugenic acid rose to the surface. After being carefully dried with chloride of calcium, its boiling-point was found to be 251° (483°·8 F.). During the distillation of some ounces, the mercury only varied 2° Cent. Ettling found its boiling-point 243° (469°·4 F.). Stenhouse's acid boiled at 242° (467°·6 F.). Dumas gives 154°, but this is doubtless a typographical error, and should be 254° (489°·2 F.). When first distilled it is perfectly colourless, but soon becomes brown even in well-filled and closely-stopped bottles. The specific gravity at 14° (57°·2 F.) was 1·0684. It had been previously determined to be 1·079. Stenhouse's acid had the density 1·076. On combustion with oxide of copper and oxygen gas I obtained the following results:—

* Chem. Gaz., April 1858.

0·2488 grm. eugenic acid gave 0·6666 carbonic acid and 0·1730 water,
0·1730 „ „ „ 0·4639 „ „ 0·1186 „

or, per cent.—

	Experiment.			Calculation.	
	I.	II.			
Carbon	73·1	73·1	C^{20}	120	73·17
Hydrogen	7·7	7·6	H^{12}	12	7·32
Oxygen	19·2	19·3	O^{4}	32	19·51

In making the combustions, it was found that a considerable deposition of carbon formed in front of the bulb, requiring a large volume of oxygen to be passed over it at the end of the analysis in order to effect its conversion into carbonic acid. The low carbon determinations of previous observers probably arose from no oxygen (or at least an insufficient quantity) being passed through the combustion tube.

When eugenic acid is boiled for a short time, it acquires a brown colour, and leaves a dark residue on distillation. This fact made it probable that the excessively high number obtained by Dumas for the vapour-density, arose from the fluid becoming decomposed in the balloon. As it was exceedingly desirable to confirm the above results, I repeated the experiment very carefully in a balloon filled with hydrogen.

Excess of weight of balloon....	0·7030 grm.
Temperature of vapour	274°
Temperature of air	18°
Pressure	758 mm.
Capacity of balloon	275·5 cub. cent.
Residual air	1·0 cub. cent.
Density	5·858

The formula $C^{20}H^{12}O^{4}$ requires—

20 vols. carbon vapour	0·8290	× 20	=	16·580
24 „ hydrogen....	0·0692	24		1·661
4 „ oxygen	1·1056	4		4·422
				22·663
				4 = 5·6657

The above determination, although yielding a number higher than that required by theory, is quite sufficient to confirm the 20 carbon formula.

On boiling eugenic acid with baryta-water, a salt is produced the stability of which contrasts strongly with the singular spontaneously decomposable compound with ammonia. It crystallizes from water and alcohol in small pearly plates of great brilliancy and whiteness. On exposure in the water-bath for some time it becomes slightly coloured. When heated to low redness, it leaves a black mass very difficult to procure white by burning. The salt was therefore boiled

with dilute sulphuric acid, and the baryta determined as sulphate. Dried at 100° (212° F.) it gave the annexed numbers—

0·5514 grm. gave 0·2805 grm. of sulphate of baryta,

or, per cent.—

Experiment.	Ettling.	Theory ($C^{20}H^{13}BaO^4$).
33·4	32·8	33·04.

These results render it certain that the formula proposed by Gerhardt for eugenic acid is correct; eugenic and cuminic acids are therefore isomeric.

It is well known that the acid in clove-oil is accompanied by a hydrocarbon said to be isomeric with oil of turpentine. The boiling-point and density are, however, very different. According to Ettling, the boiling-point is 143° (289°·4 F.). I find that of a very carefully prepared specimen to be 251° (483°·8 F.). Its specific gravity at 14° (57°·2 F.) was 0·9016. Ettling found it at 18° (64°·4 F.) 0·918. The oil as obtained by me has none of the pungency of oil of turpentine, and it is much less fluid. Its comparative insolubility in alcohol is also quite sufficient to distinguish it. In many respects it strongly resembles the oils of copaiva and cubebs. Oil of copaiva has the density 0·91 (0·878 Gerhardt), boils at 245° (473° F.), and requires 25—30 parts of alcohol of the density 0·85 for solution. Oil of cubebs has the density 0·929, and boils between 250° and 260° (482° and 500° F.). A combustion of the hydrocarbon from clove-oil furnished the following result:—

0·1807 grm. gave 0·5811 carbonic acid and 0·1947 water,

or, per cent.—

	Experiment.		Calculation.	
Carbon	87·7	C^{20}	120	88·23
Hydrogen	11·9	H^{16}	16	11·77

With most reagents it behaves like its isomer, oil of turpentine.

On the Presence of Oxide of Silicium in the residue obtained on dissolving Pig-iron. By Professor Wöhler.

It was long since observed by Schafhäutl that the black residue left when pig-iron is dissolved in muriatic acid, when thoroughly washed with water, evolves hydrogen briskly when ammonia is poured over it. In experiments made upon this subject by Dr. Hall, this remarkable fact was fully confirmed, but the explanation then attempted has since proved to be incorrect. Thus, since the existence of an oxide of silicium which has the property of being converted into silicic acid with evolution of hydrogen when in contact with ammonia, it became probable that this black residue, from which silicic acid may be extracted, actually contains oxide of silicium. This supposition has been fully confirmed by closer investigation. The siliciuret of iron in pig-iron consequently forms not silicic acid, but oxide of silicium when dissolved, a property which it shares with siliciuret of manganese.—Liebig's *Annalen*, December 1857, p. 374.

On the Equivalents of the Elements. By M. DUMAS.

The author has presented to the Academy of Sciences a very interesting paper upon the equivalents of the elements, which not merely contains several re-determinations of the equivalents themselves, but points out remarkable numerical relations between the atomic weights of bodies belonging to the same natural group. The author gives the following as the results of his numerical determinations:—

Silver, 108	Fluorine, 19	Tungsten, 92
Chlorine, 35·5	Selenium, 40	Manganese, 26
Bromine, 80	Tin, 59	Boron, 11
Iodine, 127	Molybdenum, 48	Silicon, 21
Sulphur, 16.		

The equivalent of silver was calculated from Marignac's analyses, by taking nitrogen =14 and oxygen =8. To determine the exact number for chlorine, the author heated weighed quantities of silver in a current of chlorine gas, maintaining the temperature until the resulting chloride was completely fused. This very beautiful method requires but three weighings, and leads precisely to the number 35·5. The equivalents of bromine and iodine were determined by heating weighed quantities of bromide and iodide of silver in a current of chlorine and fusing the resulting chloride. These numbers agree with those found by Marignac. The equivalent of fluorine was determined by the analysis of a very pure native fluor spar, as well as by that of crystallized fluorides of sodium and potassium. The number 16 for sulphur was verified by burning a known weight of silver in a current of the vapour of sulphur. Direct experiments on the formation of chloride of selenium gave the number 40 for the equivalent of that element: the author thinks that the difference between his result and that of Berzelius is due to the fact that he was able to employ a purer selenium. The equivalent of tin was found by the method of Berzelius, that is to say, by heating the bichloride with nitric acid, and igniting the resulting stannic acid. The acid ignited in a matrass of hard glass gave precisely the equivalent found by Berzelius, viz. 58·8, but on ignition in a platinum crucible the oxide loses traces of water, and after this correction the equivalent becomes 59. The equivalent of molybdenum was determined by igniting molybdic acid in a current of hydrogen, and was found to be 48. The equivalent of tungsten was determined in a similar manner. In the case of manganese the number 26 was found by igniting an artificial binoxide in a current of hydrogen so as to reduce it to protoxide. The number 11 for boron is calculated from recent analyses of the chloride by Deville; that of silicon was determined by analyses of the chloride, and found to be between 21 and 21·2. The author found it, however, impossible to remove from the chloride traces of chloroxycarbonic acid which it holds in solution, and the presence of which is easily shown by agitating the chloride with water when carbonic acid gas is disengaged.

The author is still engaged with the subject of a revision of the

equivalents, and the publication of his results, which cannot be looked for till the close of the present year (1858), will be awaited by chemists with special interest.

In order to exhibit the numerical relations between the equivalents of the different elements, the author, after referring to the previous investigations of Prof. Cooke, takes up in the first place the examination of certain groups and series presented by organic chemistry. If we consider the homologous series $C^3 H^3$, $C^4 H^5$, $C^6 H^7$, &c., we remark at once that there is a common point of departure for and a common difference between the equivalents of the successive terms. The formula $a+nd$ represents the generation of all these radicals, a being the equivalent of the first, and d the difference between the first and second term. The author remarks that if we did not know the law of progression, we might easily be led to think that the ratio between the numbers 141 and 281, 127 and 253, 113 and 225, is the simple ratio of 1 : 2, especially as chemistry can hardly decide with absolute certainty whether an element has, for example, the equivalent 225 or 226. The formula deduced from the simple progression above mentioned would not account for the generation of the elements as Prof. Cooke supposed. But the organic radicals are not always produced by addition, but sometimes by substitution, as we see in the compound ammoniums. We may have, for instance, the following ammoniums:—

a	$a+d$	$a+2d$	$a+3d$	$a+4d$
	$a+d'$	$a+d+d'$	$a+2d+d'$	$a+3d+d'$
		$a+2d'$	$a+d+2d'$	$a+2d+2d'$
			$a+3d'$	$a+d+3d'$

$$a+d+d'+d''+d'''$$

where a represents ammonia NH^4, and d, d', &c. represent the equivalent of hydrocarbons of the series $C^n H^n$.

In the next place, there are certain radicals in organic chemistry where the fundamental molecule itself changes as well as the bodies added to or substituted in it. Thus, tin and ethyle form six molecular groups possessing all the properties of organic radicals. If we represent tin by a and ethyle by d', we have for the six species of stannethyle the formulæ

$a+d'$	$2a+d'$	$4a+d'$
	$2a+3d'$	$4a+3d'$
		$4a+5d'$

($na+nd'$) being the general formula. With these premises the author proceeds to compare the equivalents of the elements. The elements F, Cl, Br, I do not form a single progression. The relation between their equivalents is, however, exhibited by the scheme a, $a+d$, $a+2d+d'$, $2a+2d+2d'$, or in numbers,—

Fluorine.....	19
Chlorine	$19+16{\cdot}5=35{\cdot}5$
Bromine.....	$19+33+28=80$
Iodine	$38+33+56=127$.

Nitrogen, phosphorus, arsenic, antimony, and bismuth form another

natural group, and for their equivalents we have the scheme, $a, a+d, a+d', a+d+2d'$, and $a+d+4d'$, or in numbers,—

Nitrogen	14
Phosphorus	14+17=31
Arsenic	14+17+44=75
Antimony	14+17+88=119
Bismuth.....	14+17+176=207.

The author gives similar series for carbon, boron, silicon, and zirconium, as well as for tin, titanium and tantalum, which we omit. For oxygen, sulphur, selenium, and tellurium we have either of the series a, $2a$, $5a$, $8a$, or $a, a+d, a+4d, a+7d$. Analogy points out the latter as preferable, and we have in numbers,—

Oxygen	8
Sulphur.....	8+8=16
Selenium	8+32=40
Tellurium	8+56=64.

A common difference of 8 also connects Mg, Ca, Si, Ba, Pb; thus we have—

Magnesium	12
Calcium.....	12+8=20
Strontium	12+32=44
Barium	12+56=68
Lead	24+80=104.

Lithium, sodium, and potassium belong to a similar series with a common difference of 16.

Lithium.....	7
Sodium	7+16=23
Potassium	7+32=39.

Molybdenum, tungsten, chromium, and vanadium form a similar series of which the common difference is 22, the progression being 26, 48, 70, 92. The author considers his results as favourable to the idea of Dr. Prout, who supposed the equivalents of all the elements multiples by a whole number of that of hydrogen. In the case, however, of chlorine, and perhaps of some other elements, the unit of reference is less than the equivalent of hydrogen and is probably 0·5. In all the series the first member determines the chemical character of all the other terms. These considerations, the author remarks, will have more weight when he presents the study of a natural family of which hydrogen is the first term, and exhibits the connexion between the physical properties of the elements, and the position which each occupies in the series of which it forms a member.—*Comptes Rendus*, Nov. 1857, xlv. p. 709; and Silliman's *American Journal*, March 1858.

On the Products furnished by Sugar and Starch when heated.
By A. Gélis.

Cane-sugar is converted by heat into so-called caramel. If the latter be extracted in the cold with alcohol of spec. grav. 0·848,

the whole sometimes dissolves. If this solution be evaporated, there remains a brown syrup of a bitter taste. It still contains the sugar which escaped conversion; the metamorphosed body itself is called caramelan by the author. All the properties by which the so-called caramel is distinguished from sugar belong to this caramelane, as well as that of attracting moisture from the air. Its composition is $C^{18} H^{8} O^{8}$, HO.

The higher the temperature at which the caramel was prepared, the more does it furnish of a second body, which is insoluble in alcohol of spec. grav. 0·848. If this residue be extracted with water, another substance is dissolved; this the author calls caramelene. It combines with bases, with even more facility than caramelane. Its composition is $C^{36} H^{24} O^{24}$, HO.

The residue, which is insoluble in water and alcohol, contains a third product of metamorphosis, which the author calls carameline. Its composition is $C^{96} H^{50} O^{50}$, 2HO. It may be obtained in three states:—1. soluble in water; 2. insoluble in water, but soluble in some other solvents; 3. completely insoluble.

Carameline occurs in the first and second conditions in the residue, which is left by caramel after extraction with cold water. The modification 2 may be obtained therefrom by means of hot water and alcohol of spec. grav. 0·912.

If the residue which contains the carameline be treated with boiling water, a strongly coloured fluid is obtained. In the production of this two things are to be distinguished. In the first place, independently of the action of the boiling water, the modification 2 is converted into the soluble one. When once a solution has been obtained, it remains coloured even when concentrated. As it evaporates it becomes covered with a film, and this is now no longer the first modification of carameline, but it is again 2, into which the soluble carameline has been converted.

The modification 1 is also converted into the insoluble 2, when the solution is precipitated by alcohol. The fluid becomes almost decolorized, and the deposit is carameline No. 2.

The solutions of carameline in water mixed with ammonia or potash, let fall precipitates on the addition of acids, like alkaline ulmates. At the first moment these precipitates are nothing but the modification No. 2 of carameline, which, however, after standing for several days in the moist state, and also when dried, passes into the modification No. 3. Carameline can consequently only be obtained from quite freshly prepared caramel, and for the same reason the vessels in which solutions of caramel are kept, always become covered with an insoluble brown stratum.

The carameline B is insoluble in cold water and strong alcohol, but dissolves in a mixture of equal parts of water and alcohol.

All these bodies furnished by cane-sugar, when heated, are produced from the sugar by its losing water. Grape-sugar furnishes similar, but not identical products.

The changes which starch undergoes when heated were observed by Vauquelin as early as 1811, and products of this nature are

already objects of commerce and employed in the arts, under the denominations of leiocome and dextrine.

In order to study the changes which starch undergoes when heated, the author exposed it to high temperatures in a flat-bottomed pot, heated from the side. It first loses water, becomes converted into dextrine, and begins to acquire colour. It then fuses as it were, and becomes inflated. By suitable stirring of the spots not sufficiently heated, the entire contents may be gradually converted into a strongly coloured and almost completely fused mass.

This mass is then extracted with water. Imperfectly metamorphosed and burnt starch remains in the residue. The solution is evaporated, spread out in thin layers, and dried at 452° F. A light spongy mass is obtained, which may be easily reduced to powder. It is unalterable in the air, very readily soluble in water, and furnishes a brown solution. The pure substance which forms the essential constituent of this is called pyrodextrine by the author.

If some dextrine is still intermixed in the substance, this may be easily got rid of by precipitation with alcohol. If it contains other matters, they are thrown down by baryta-water. Dextrine is not precipitated by baryta. Pyrodextrine, on the contrary, is precipitated by baryta, especially when about a tenth of alcohol is added to the fluid.

Pyrodextrine occurs in crusts of bread. To obtain it from this and similar substances, which contain it only in small quantities together with other starch-like and saccharine matters, the starch is converted into sugar by malt or sulphuric acid, the sugar destroyed by fermentation, and the pyrodextrine thrown down by means of baryta.

To obtain the pyrodextrine from the baryta precipitate, the latter is decomposed by sulphuric acid, and the acid fluid is saturated with carbonate of baryta. It is then filtered and evaporated.

The pyrodextrine thus obtained is a solid, black mass, shining, and elastic like gum when it is not perfectly dry. It is tasteless, inodorous, unalterable in the air, insoluble in strong alcohol, nearly soluble in aqueous alcohol, insoluble in æther, and very soluble in water. The brown solution has three times the colouring power of caramelene.

Dextrine is converted by heat into pyrodextrine with loss of water; and whilst the former contains 12 equivs. of carbon, the formula of pyrodextrine is $C^{48} H^{36} O^{36}$, HO.

Dextrine does not appear to furnish anything but pyrodextrine when heated. It occurs in all amylaceous substances, altered by baking, in crust of bread, roasted malt, coffee, &c.—*Comptes Rendus*, xlv. pp. 590 and 988.

New Observations on the Preparation of Manganese.
By C. Brunner.

The author adds the following observations to his previous statements published last year with regard to the preparation of manganese.

Wöhler observed that a sample of manganese sent to him by Brunner, when dissolved in muriatic acid left a whitish residue, and ascertained that this residue was the hydrated oxide of silicium discovered by him. He concluded from this that it was due to silicuret of manganese, and that its more ready fusibility, observed by Brunner, was caused by this contamination.

Brunner found this opinion to be correct, and endeavoured to ascertain,—

1. Whether this presence of silicium was a necessary consequence of the mode of preparation, and

2. Whether the amount of silicium could be diminished in any way.

The examination of manganese from different preparations showed that the amount of silicium was very variable in it; in 12 samples the amount of its oxide varied from 1·6 to 6·8 per cent.

The author also succeeded in increasing the amount of silicium, by fusing the metal with silica and chloride of sodium, or by adding some silicofluoride of potassium during the reduction. In this way he increased the amount of silicium to 9·86 per cent.

It was far more difficult, however, to diminish the amount of silicium. This was best done in the following manner:—The reduced metal was coarsely pounded in the steel mortar, and then mixed with twice its weight of anhydrous chloride of sodium, to which 1 per cent. of chlorate of potash had been added. It was then fused at a white heat, which was maintained for 8—10 minutes.

In this way the amount of silica was reduced to one-thousandth. The properties of the manganese did not appear to be altered by this amount; the colour, fusibility, hardness, and lustre remained the same.—Poggendorff's *Annalen*, ciii. p. 139.

ANALYTICAL CHEMISTRY.

On the Separation of Tantalic Acid from the Acids in the Columbites. By F. Oesten.

The author has further tested Hermann's process* for separating tantalic acid from the other metallic acids contained in the columbites. He proceeded exactly in accordance with Hermann's directions, and employed the quantities of the A-sulphates of these acids, and of the solvents recommended by Hermann:—to a quantity of the A-sulphates containing 20 grains of anhydrous acids, 1 ounce of solution of soda containing $\frac{1}{4}$th of hydrate of soda. After boiling with this solution, 12 ounces of water are added, and the whole is again boiled. If only the acids of niobium were present, the solution should be clear according to Hermann; if tantalic acid be present, a turbid fluid is produced. This is filtered, and the separated tantalic acid is collected on the filter, which is then burnt, and the residue is fused with bisulphate of potash, to which a little fluoride of sodium has been added, in order to volatilize the silica of the filter. After washing the fused mass, pure tantalic acid remains.

* Chem. Gaz., vol. xv. p. 10.

When tantalic acid is present at all, it always coexists in the solution of soda with the other acids; it is separated as far as possible by repetition of the same operation.

The author has treated the acids of several columbites in accordance with this process, but never obtained an insoluble residue (tantalic acid). This was the case with the acids from the columbite of Bodenmais of spec. grav. 5·385 and 5·403, with the acids from that of Greenland of spec. grav. 5·856, from that of Middletown of spec. grav. 6·101, and from that of the Ural of spec. grav. 4·70.

The tantalic acid from the tantalite of Kimito left 25·15 per cent. undecomposed; 74·85 per cent. were therefore dissolved by boiling with solution of soda. After cooling, nearly all the tantalic acid separated as tantalate of soda, but dissolved again on the application of heat. The acid dissolved by the hydrate of soda, when perfectly purified, had a spec. grav. of 7·234.

Of the tantalic acid from the tantalite of Tamela prepared pure from the chloride, 80·55 per cent. were dissolved, and only 19·45 per cent. remained undissolved. The spec. grav. of the dissolved portion was 7·244.

From this it is evident that the tantaloid acids cannot be separated by hydrate of soda. Tantalic acid indeed separates pretty completely from the cold solution, but the acid of the columbites does not remain entirely dissolved in the solution of soda. Columbic acid is completely soluble in the boiling solution of soda, but the greater part of the tantalic acid is also dissolved. The columbite of Bodenmais appears to contain no tantalic acid.—Poggendorff's *Annalen*, ciii. p. 184.

Process for distinguishing Sulphured Hops from those which have not been treated with Sulphur. By Prof. RUDOLPH WAGNER.

Nitroprusside of sodium is dissolved in water. The solution should be diluted until it only appears of a faint brownish colour, and then mixed with a few drops of solution of potash.

In other respects the process is the same as that of Heidenreich; the hops to be tested are put into the flask with a few fragments of zinc-foil, dilute muriatic acid is poured over them, and the gas evolved is conducted into the alkaline solution of nitroprusside. If even the least quantity of sulphuretted hydrogen is mixed with the hydrogen gas, the first gas-bubble causes a small violet cloud in the fluid; after the gas has been passing for a short time, the solution acquires the beautiful colour of permanganate of potash. The vapours of muriatic acid carried over with the gas do not interfere with the reaction, when the passage of the gas through the fluid is not continued too long. As a matter of course, the gas must not be washed; the utmost that can be done is to filter it through a plug of cotton wool.

In hops which had been purposely treated with sulphur no trace of sulphurous acid could be detected after the lapse of a few months. —*Archiv der Pharm.* xcii. p. 301.

THE CHEMICAL GAZETTE.

No. CCCLXXIV.—May 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Preparation of Pure Compounds of Cerium.
By R. BUNSEN.

THE remarkable property of protoxide of manganese, of being converted by ignition with magnesia or oxide of zinc with access of air into peroxide, which combines with the stronger base to form a compound unalterable by heat, and may be separated from this by dilute acids, rendered it very probable that oxide of cerium would also exhibit a similar behaviour. The confirmation of this supposition appeared the more important, as the hitherto unsuccessful preparation of solutions of peroxide of cerium, free from protoxide, furnishes, almost of itself, a simple and more certain way of separating cerium from the other metals associated with it. The author has therefore induced Vogler to make some experiments on this subject, which led to the following method for preparing perfectly pure compounds of cerium in the simplest way.

1 part of finely pounded cerite is as usual stirred with concentrated sulphuric acid into a stiff paste and heated. The mass swells considerably, and after the completion of the action, a gray powder is obtained, containing the earths and oxides of the mineral in the form of sulphates. This is put into a Hessian crucible and exposed to a red heat until a sample taken out furnishes with water a solution free from iron. The sandy powder, which is now red, is extracted, first with water and then by heating with dilute nitric acid. If the solution still contains iron, this is thrown down by careful neutralization with carbonate of soda; the remaining fluid is then freed from copper, bismuth, and molybdenum, which are usually present in it, by means of sulphuretted hydrogen. The solution, which, besides the oxides of the cerite, now only contains some phosphoric acid, lime, yttria, and magnesia, may be used directly for the separation of the cerium. It is mixed with a weight of sulphate of magnesia free from iron, equal to that of the cerite employed, heated to boiling, and precipitated with carbonate of soda. The precipitate, washed by decantation and dried, is slightly calcined for two

or three hours, when all the protocarbonate of cerium contained in it is converted into peroxide, which dissolves readily and completely with the other oxides in concentrated nitric acid when heated, forming a deep brownish-red fluid. Besides a small quantity of nitrate of yttria, this contains a double salt of pernitrate of cerium and didymium with nitrate of lanthanium and magnesia; it is obtained in beautiful rhombohedric crystals, and possesses almost the intense colour of bichromate of potash. The rhombohedra, which exhibit the combination R—OP, form terminal edges of about 84°, and may be dissolved in water and recrystallized without decomposition.

The solution from which these crystals are deposited, after dilution with water, is not precipitated either in the cold or when boiling. If the rhombohedra be allowed to crystallize until only laminar crystals of a paler colour, containing magnesia, oxide of lanthanium, and a very little oxide of cerium, separate, a basic salt of cerium is thrown down even by the mere boiling of the dilute mother-liquor; this, however, dissolves again on the addition of a solution of the red rhombohedric crystals, and is consequently not produced so long as these red crystals are still in solution. This precipitate, notwithstanding the peculiar conditions under which it is produced, possesses, after calcination, all the properties of a pure compound of cerium.

To separate the cerium from the red solution in nitric acid, it is diluted with much water, heated to boiling, and mixed with a small quantity of sulphuric acid, so long as the resulting precipitate increases in quantity. The cerium is thus immediately thrown down in a perfectly pure state as a basic persalt, in the form of a yellowish-white flocculent mass, which is washed with difficulty upon a filter, but readily and completely by decantation with hot water containing some sulphuric acid.

The compound of cerium thus obtained, which contains sulphuric and nitric acids, dissolves readily in more concentrated acids to form a yellow solution, which, when reduced by sulphurous acid, and precipitated from the acid solution by oxalic acid, furnishes chemically pure protoxalate of cerium. This, when ignited in the air, leaves a white protoperoxide, with a scarcely yellowish tinge; this may be converted into a salt soluble in water by treatment with hot concentrated sulphuric acid, but is only slightly acted upon by muriatic acid, nitric acid, and dilute sulphuric acid. When calcined with magnesia, this oxide usually becomes only partially soluble again, indicating that the presence of oxide of lanthanium with the magnesia is necessary to effect the conversion into peroxide.

The fluid from which the peroxide of cerium has been separated is usually coloured of a deep reddish-violet by a higher oxide of didymium, and resembles a solution of permanganate of potash. On the addition of alcohol, or tartaric acid, on filtration through bibulous paper, and generally in the presence of reducing agents, this colour instantly disappears. The solution separated from the preci-

pitate of cerium still contains much cerium, which may be obtained by the repetition of a similar process to that just described.

If the nitric solution, which now contains principally lanthanium, didymium, and magnesia, be evaporated, a very beautiful double salt of these bases is obtained, forming crystals of an inch in length, and constituting the starting-point of a series of double nitrates.

J. Jegel has continued Vogler's experiments, and essentially simplified the method described. The original extract of the oxides of cerite *not* heated to redness, when treated with sulphuretted hydrogen, may be still more simply precipitated at once by oxalic acid, after the addition of *a considerable quantity* of muriatic acid. The oxalates obtained, which are perfectly free from iron, form a caseous precipitate, which very rapidly becomes granular, and may then be washed by decantation almost as easily as chloride of silver. This is dried, and triturated with half its weight of moist, pure *magnesia alba* to a stiff paste, and this after being dried is heated in a porcelain capsule, of which the bottom is very slightly reddened over an open charcoal fire, and constantly stirred for some time, when a cinnamon-brown powder is obtained; this contains all the cerium as peroxide, and dissolves readily in hot nitric acid to form a red fluid, which may be employed, as above described, for the separation of the peroxide of cerium. If this oxide, as is often desirable, is to be prepared free from sulphuric acid, and only containing nitric acid, it is sufficient to evaporate the red solution to the consistence of a syrup, and pour it into a great excess of boiling water containing some nitric acid. The precipitated basic pernitrate of cerium is washed by decantation with hot water containing some nitric acid; the washing-water and the mother-liquor are again evaporated to the consistence of a syrup, and again treated in the same way until nearly all the peroxide of cerium is separated. The addition of some acid to the washing-water is absolutely necessary, as the precipitated basic salts are tolerably soluble in pure water. They are best preserved under water, as they become insoluble in acids after being dried or calcined.—Liebig's *Annalen*, January 1858, p. 40.

On some of the Products of the Destructive Distillation of Boghead Coal.—Part I. *By* C. Greville Williams, *Lecturer on Chemistry in the Normal College, Swansea.*

The action of heat on organic substances has been studied under two aspects: in the one the relation of the products to the original matter is seen, and we are enabled to draw theoretical deductions, in most cases of great simplicity; in the other, the relation is not capable of being traced; and it would appear, therefore, at a first glance, that the study of bodies produced in this manner would be less conducive to the advancement of theoretical science. But so far from this holding good, it is not too much to assert that organic chemistry has been more enriched by products of the second kind than the first. The metamorphoses of naphthaline, to which the law of substitution owes so much for its development; the study of aniline,

which has so greatly increased our knowledge of the theory of basic combinations; the history of the phenyle series and its numerous homologues,—are, immense as their influence on the progress of chemistry has been, only a few instances of what may be anticipated from the study of products of destructive distillation. It is true that their history has been developed, not because of their origin, but from their intrinsic interest, yet it cannot be denied that no operation has furnished chemistry with products so numerous and diversified in character. It is also unquestionable that no organic type exists unrepresented by bodies of pyrogenous derivation.

Heat is perhaps the only chemical agent to which we can assign no special function; at one time acting as a powerful incentive to oxidation, at another to reduction; it is generally recognized as the most potent of disruptive forces, yet we sometimes find it causing the coalescence and reduplication of atoms; it is evident, therefore, allowing heat to possess these various and apparently antagonistic qualities, that there are few organic bodies capable of withstanding high temperatures whose presence among products of destructive distillation can be looked upon as impossible. The progress of chemical science has moreover shown in repeated instances, that the substances at one time regarded as the rarest and most difficultly obtainable, become in a short period those with which we are most familiar. The present investigation may be considered a case in point, its object being to prove the existence in great quantity in a commercial product, of a class of compounds hitherto only procurable by processes founded on purely theoretical considerations, and requiring considerable care in their prosecution.

The substance, the distillate from which contains the hydrocarbons forming the subject of this communication, is the Torbane-hill mineral or Boghead Coal, worked on a large scale at Bathgate, near Edinburgh. A very partial examination of it has been published by Dr. Genther*, with results which, as we shall afterwards see, are far from correct; for he has assumed that the fractions obtained at particular boiling-points are homogeneous, and consist of different but isomeric hydrocarbons of the formula $C^n H^n$. In addition to paraffine, long known as one of the products, he has detected picolnie and phenole; but, nevertheless, his results, on the whole, are rather in favour of the view that the Torbane-hill mineral is not a true coal in the sense generally understood by chemists. I do not enter here upon the much-disputed and litigated question of the nature of the mineral itself, my object being solely to study the chemical relations of the bodies produced by its decomposition under the influence of heat.

The ordinary Boghead naphtha appears in commerce in the form of a nearly colourless fluid of a very characteristic odour, quite different to that obtained from ordinary coal. Its specific gravity is only 0·750 at 15°, and is therefore much lower than that from the latter source, for even thoroughly purified benzole has a density of 0·850. Notwithstanding its small density the boiling-point was

* Liebig's Annalen, xcvii. p. 277; and Chemical Gazette, 1856, No. 330.

high, the lowest fraction that could be obtained in the first rectification being between 143° and 148° Centigrade. That the fluid was a mixture of many bodies of very different boiling-points, was shown by the fact that during the first distillation the mercury in the thermometer steadily rose to the highest range it was safe to allow. This complexity was still better seen by the sudden depression of the boiling-point of the first fraction in the second distillation, for there was then obtained a considerable quantity of fluid between 121° and 126°, the second rectification thus causing a fall of no less than 22°; subsequent to this, the lowering of the initial fraction with the advance in the number of rectifications was less marked, but still decided, and after six distillations I was able to procure a portion boiling as low as 98°·5.

It appearing evident that previous to attempting any examination, it would be essential to obtain the crude hydrocarbons of nearly constant boiling-point, they were submitted to a tolerably complete fractionation, during which there were made, altogether, no less than one thousand distillations.

An opinion has been hazarded by some persons, that in processes of fractional distillation a continual breaking up is taking place, which they suppose to account for the variations in the point of ebullition: that the supposition is incorrect will be admitted by all chemists who have given close attention to processes of this kind, and the question is placed beyond doubt by the fact that the variation becomes less as the distillations are more numerous, and, at last, the fractions distil almost entirely between the points at which they last came over, and doubtless might, if sufficient time was expended on them, be obtained perfectly steady.

As soon as by the means described fractions were obtained of almost constant boiling-points, I proceeded to ascertain whether the fluids consisted of more than one substance, and passing over the preliminary trials, it was soon found that more than one series of bodies were present. This was proved by the deportment of the mixed hydrocarbons with fuming nitric, or a mixture of nitric and sulphuric acids. If, into a flask of 3 or 4 ounces capacity, 2 drachms of fuming nitric acid be poured, and 1 drachm of the naphtha be added by small portions, with constant and brisk agitation, allowing the temperature to rise a little, but preventing it going too far by immersing the flask (still kept in motion) in very cold water, a point is reached when the temperature no longer rises, and it is seen that the mixture forms an emulsion of a red-brown colour, a layer of green but brilliant fluid floating on the surface; the whole is then poured into a very narrow conical glass and allowed to rest for a few minutes, by which time the fluid unacted on has risen to the surface. The lower portion having been removed and thrown into water by means of a pipette, furnished with a hollow caoutchouc ball to avoid suction with the lips, the indifferent hydrocarbon is transferred to a flask having a well-fitting stopper and containing a quantity of highly-concentrated nitric acid. When the above operation has been repeated until sufficient of the hydrocarbon has been

accumulated in the flask, the latter is violently shaken to thoroughly mix the fluids, and on standing for some time separation into two layers takes place; the lower, consisting of the acid, which has abstracted the chief part of the hydrocarbons removeable by it, is withdrawn by means of a pipette, and the operation is several times repeated. It is absolutely essential to correct results that this treatment be sufficiently performed. The acid being removed for the last time, the fluid is washed with a solution of caustic potash, which, by absorbing the nitrous fumes, removes the green colour. The indifferent hydrocarbon is then digested with sticks of potash to remove the water, and when apparently dry, is distilled several times over sodium.

The fluids obtained as above are perfectly colourless, of a pleasant odour, resembling may-blossoms, very volatile, even at low temperatures, and having a density of about 0·725. If pieces of sodium be rapidly cut from a mass, so as to have only a very thin layer of soda, and are then thrown into the perfectly dry hydrocarbon, the coating of oxide is dissolved, the metal appearing of the lustre of silver, and may probably be thus kept for any length of time.

My first experiments were made upon the fraction boiling between 115° and 121°, merely because that happened to be the largest, and it soon became evident that the hydrocarbon obtained by the process described, possessed the composition and the same degree of condensation in the state of vapour as butyle (valyle of Kolbe) But as it is evident that the formula $C^{16} H^{18}$ corresponds also to the hydruret of the radical of the caprylic alcohol, it was necessary to ascertain the correct boiling-points of the bodies obtained, because if coinciding with those of the radicals, it would be strong evidence of their identity with them. But the composition of the radicals differing but little, it is evident that analysis alone, however carefully made, cannot decide the question; fortunately, however, the addition or subtraction of $C^2 H^2$ has a very considerable influence on their vapour-density, as will at once be seen by reference to the annexed Table, where the increase is compared with the rise of carbon and diminution of hydrogen as the boiling-point becomes higher.

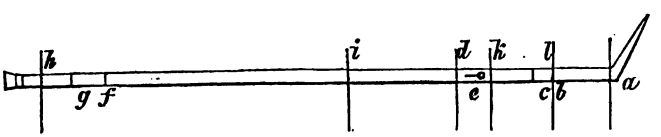
		Boiling-point.	Vapour-density.	Per-centage of carbon.	Per-centage of hydrogen.
Propyle	$C^{12} H^{14}$	65°	2·98	83·72	16·28
Butyle	$C^{16} H^{18}$	106°	3·94	84·21	15·79
Amyle	$C^{20} H^{22}$	158°	4·91	84·51	15·49
Caproyle	$C^{24} H^{26}$	202°	5·88	84·70	15·30

The boiling-points of the indifferent hydrocarbons being such important evidence, it has been considered proper to give positive proof that the fractions analysed were those whose constitution exactly tallied with the bodies with which they were sought to be identified; in each case therefore the vapour-densities of several fractions near the known boiling-point of the radicals were determined; and it is submitted, that it is no slight proof of the correct-

ness of the view advanced relative to the nature of the bodies isolated, that in almost every instance the fraction which gave the correct vapour-density was that which corresponded in boiling-point with the radical. In order to save space, the numerous determinations made are condensed into Tables. In one or two of these merely trial experiments, it will be observed that the regularity of the series is slightly interrupted; where this happens, it will be found to arise from the fact of the bodies not having been obtained from the fraction corresponding to their own boiling-point; thus in the Table containing the amyle experiments, the fourth and sixth determinations are not in perfect harmony with the rest; in the third, the fraction used distilled between 160° and 165°, but it was obtained from the portion of the crude hydrocarbons boiling between 150° and 160°; this makes the density come out somewhat lower than it would have been had the fraction been extracted from the hydrocarbons boiling between 160° and 165°. In general, however, it will be found that the increase of density with the rise of boiling-point is quite as steady as could have been anticipated.

It has been stated that the composition of the fractions varied so little as the boiling-points became higher, that I did not imagine myself justified in considering the nature of any fraction established by the mere results of analysis; but although vapour-density has been chiefly relied on as the means of research, it is believed, nevertheless, from the extreme care with which the combustions were made, that they represent very nearly the true per-centages of carbon and hydrogen.

Chemists are aware that the accurate analysis of volatile fluids, having a high per-centage of carbon, is a somewhat fatiguing process, from the constant attention indispensable, and the slowness with which it is necessary to advance the fire along the tube. By the following method of burning, which is described in the hope that it may be found useful to others, less time and far less attention are required for the determination of the carbon and hydrogen in a body like propyle or butyle, than for the combustion of an ordinary solid. For this purpose the fluid is contained in one bulb, and is driven out at the commencement of the analysis into a column of thirteen or fourteen centimetres of cold oxide of copper: this latter portion is never directly heated until the end of the analysis, the fluid being volatilized by the heat conducted by the oxide. Oxygen is, of course, passed over the reduced metal to remove any carbon which may have combined with it. The tube is arranged as in the annexed sketch.



At *a* is placed a small plug of recently ignited asbestos, about 2 centimetres long; then a mixture of fused and powdered chlorate

of potash and oxide of copper as far as *b* (about 7 centimetres); then at *c* 2 centimetres of asbestos, followed to *k* by the same length of coarse-grained oxide of copper. The substance is placed at *e*, the tube to *f* being filled completely by granular oxide of copper of about the coarseness of ordinary gunpowder, and, finally, at *g* is placed another plug of asbestos. The combustion is commenced by heating the end *a* to redness, and between the screens *h* and *i*; when fully red, the space between the screens *k* and *l* is filled with live coals, the whole of the fluid being immediately driven amongst the oxide of copper occupying the space from *d* to *i*. In a short time this oxide becomes sufficiently hot to cause a perfectly steady distillation of the fluid over the red-hot column of oxide from *i* to *h*, where it is burnt. No further attention is requisite until carbonic acid ceases to enter the bulbs, when the screen *i* is removed back; but it is always found, if the fluid is moderately volatile, that very little remains. When the tube is red-hot from *h* to *l*, the mixture of oxide and chlorate is slowly heated to redness. Combustions made in this manner seldom fail to yield good results. One great advantage of the method is, that if the space from *i* to *d* be of the proper length, there is no fear of either a sudden rush of gas or of the operation being tediously slow. All the fluid analyses given in this paper were made in this manner.

On the Hydrocarbons unacted on by Sulphuric and Nitric Acids.—The lowest fraction obtained during the rectifications was between 65° and 71°; the quantity was far from large; and although working on a tolerably extensive scale, great care was requisite to prevent loss by evaporation during the distillations. The density at 15°·5 of the crude hydrocarbons was only 0·735, although containing a considerable per-centage of benzole. On treatment with highly concentrated fuming nitric acid, in the manner previously described, and placing the acid and nitrocompound in a conical glass, for the purpose of facilitating the separation of the hydrocarbon unacted on by acids, I was surprised to find that no separation whatever took place; and on throwing the mixture into water, no nitrocompound fell to the bottom, the whole rising to the surface in the form of a pale green layer. The latter was therefore separated, placed in a retort, and the heat of a water-bath applied; a considerable quantity of a colourless fluid distilled over, which was treated several times with fuming nitric acid to remove any of the other hydrocarbons present, the last traces being retained with such tenacity that the process had to be repeated many times before the separated acid no longer produced milkiness when thrown into water, indicating the presence of the nitrocompound. After washing several times with solution of potash, and digestion with sticks of the latter substance to remove moisture, it was distilled over fragments of sodium, and came over chiefly between 65° and 71°. On one occasion, when distilling over sodium some impure propyle, as soon as the retort became nearly dry, a small quantity of nitrocompound present, which had dissolved in the indifferent hydrocarbon, reacted on the metal with great violence, the latter becoming ignited, tor-

rents of smoke being evolved, and large quantities of carbon at the same time depositing on the interior of the retort and receiver: when the radical is in a state of purity, sodium remains perfectly brilliant under it during the distillation.

In order to ascertain the boiling-point of propyle, I commenced by determining the vapour-density of the fractions, beginning with the portion distilling, in the sixteenth rectification, between 72° and 79°: the experiments were made by the method of Dumas, the second being taken at a slightly higher temperature than the first.

	I.	II.
Temperature of air	20°	20°
Temperature of vapour	104°	112°
Pressure	769 mm.	769 mm.
Excess of weight of balloon..	·4673 grm.	·4817 grm.
Capacity of balloon	294 cub. cent.	307 cub. cent.
Residual air	11 cub. cent.	5 cub. cent.

Experiment.		Theory.
I.	II.	$C^{12}H^{14}$=4 volumes.
3·10	3·08	2·97

It appearing, therefore, that the boiling-point was considerably below 79°, the fraction distilling between 65° and 70° was taken for further examination. On combustion, it furnished—

	Calculation.		Experiment.	
			I.	II.
C	12=72	83·7	83·7	83·7
H	14 14	16·3	16·7	16·3

The following are the details of a determination of the vapour-density of the same portion of fluid by Gay-Lussac's method:—

Weight of fluid	·1098 grm.
Temperature of vapour	100°
Observed volume of vapour	43·5 cub. cent.
Atmospheric pressure	772·1 mm.
Difference of mercury level	85·4 mm.
Density of vapour	2·956

The formula $C^{12}H^{14}$=4 volumes requires—

12 volumes carbon vapour..	0·8290 . 12=9·948
28 volumes hydrogen	0·0692 . 28 1·938
	$\frac{11·886}{4}$=2·972

Experiment.	Theory.
2·956	2·972

The substance unacted on by acids boiling at 65°, as extracted from the Torbane-hill mineral distillate, has therefore not only the composition, but also the vapour-density of the radical of the propylic series. I shall show, further on, that its boiling-point also

coincides with what might be expected. It is evident that propyle might be procured by electrolysis of butyric acid, and I propose eventually to subject the hydrocarbons from both sources to a careful comparison. It may be mentioned that propyle has not previously been obtained. Its density at 18° was found to be 0·6745.

Nitrocompound from Fraction boiling between 66° *and* 71°.—This substance, which, it has been said, floated on water while holding the radical in solution, was much heavier than that fluid after the hydrocarbon had been distilled off. Treated with alcoholic potash great heat was produced, the solution becoming blood-red, and a peculiar odour being evolved. The mixture was placed in an iron alembic, and the alcohol distilled off on the water-bath; the latter was then removed, and the distillation continued over the naked fire. An abundance of milky fluid containing an alkaloid came over, accompanied by a small quantity of non-basic oil. At last an explosive evolution of vapour ensued; the chief portion of the contents of the alembic being projected into the neck, and there becoming solidified, stopped the distillation. The non-basic oil was removed by addition of hydrochloric acid to dissolve the base, and then passing through a wet filter. The undissolved portion solidified on the filter to a mass of golden-brown crystals having the characters of azobenzide. A large quantity of aniline was found in the basic portion of the distillate. The nitrocompound contained, therefore, a considerable amount of nitrobenzole. The study of the nitrocompounds and their products is reserved for a future communication.

[To be continued.]

On the Behaviour of Boracic Acid to Tartaric Acid.

By H. Rose.

It is generally supposed that in the compounds of cream of tartar with boracic acid and borax, the boracic acid plays the part of a base towards the tartaric acid. There are, however, many facts which speak against this supposition.

When boracic acid is dissolved in alcohol, the solution burns, as is well known, with a green flame. In this case the formation and volatilization of borate of oxide of æthyle causes the green colour of the flame, for if the boracic acid be combined with a strong base, it loses the property of communicating a green colour to the flame of alcohol. This only appears when a strong acid, especially sulphuric acid, is added.

Several organic acids, but especially tartaric acid, behave in this respect as strong bases towards boracic acid; they deprive boracic acid of the property of burning with a green flame in its alcoholic solution. It requires a considerable quantity of the organic acid, however, to produce this action; to 1 equiv. of boracic acid not less than 10 equivs. of crystallized tartaric acid must be employed. If such a mixture be dissolved in alcohol, the solution, when in-

flamed, does not burn with a green colour. But if sulphuric acid be added to the alcoholic solution, the green colour immediately appears, just as when this acid is added to the compounds of boracic acid with strong bases.

Amongst inorganic acids only phosphoric acid behaves something like tartaric acid towards boracic acid. But larger quantities of phosphoric acid are necessary to obtain the same result that is produced by small quantities of tartaric acid. The green flame is also produced in this case by the addition of sulphuric acid.

The various compounds of borax and cream of tartar also only give a green colour to the flame of alcohol when sulphuric acid has been added.

In numerous investigations upon the expulsion of the basic water from crystallized tartaric acid by means of boracic acid, no other result could be obtained, but that boracic acid is incapable of producing this effect; so that it never exhibits even such weak basic properties as water.

In order to determine with some degree of certainty which of the two acids (tartaric and boracic) may be regarded as the base in their compounds, the latter was submitted to the action of the voltaic pile. A solution of 1 equiv. of boracic acid and 10 equivs. of tartaric acid, which did not burn with a green flame on the addition of strong alcohol, was placed in the circuit of a pile which only consisted of two Grove's elements, in order to prevent the decomposition of the tartaric acid. The poles were composed of strips of platinum, and separated from each other by an earthen cylinder. After the lapse of a few hours the fluid from the two poles was examined, when that from the positive pole burnt with a strong green flame on the addition of strong alcohol; this was not the case with that from the negative pole, except after the addition of sulphuric acid. From the result of this experiment it is hardly possible to regard boracic acid as the base in its compound with tartaric acid.

Racemic acid behaves in all points like tartaric acid towards boracic acid.

The property of boracic acid of rendering turmeric-paper brown, has also furnished a reason for regarding it as a base. The brown colour produced by boracic acid upon this test-paper, has, however, no similarity with that caused by alkaline solutions. The latter is produced immediately after the immersion of the paper; it is then very strong, even with weak alkaline solutions, and decidedly brownish-red, but in drying acquires a different tint, shows a tinge of violet, and if the alkaline solution was very weak, it disappears almost entirely some time after the immersion. This is the case, for example, when turmeric-paper is dipped into lime-water.

On the other hand, the brown colour which is produced upon turmeric-paper by an aqueous or alcoholic solution of boracic acid, is not to be observed after immersion, and only makes its appearance when the paper is dried. It is then weak, but still characteristically brownish-red. It is, however, remarkably strengthened

when the solution of boracic acid is mixed with another acid, and then dried upon turmeric-paper. All acids have this action, but the stronger, acids as muriatic acid, nitric acid, and even tartaric acid, but especially dilute sulphuric acid, in a far higher degree than the weaker acids, such as acetic acid, which, of themselves, have no action upon turmeric-paper. After complete desiccation the paper then appears of a clearer and very strong red.

That the brown coloration of turmeric-paper by alkaline solutions and boracic acid stand in no connexion with each other, is shown also by the behaviour of solution of borax towards turmeric-paper. The latter, when immersed in solution of borax, immediately becomes brownish-red with a weak alkaline solution, but this colour disappears almost entirely after the drying has been effected for a considerable time, or it only leaves a very weak reaction produced by boracic acid. Solution of borax, therefore, behaves towards turmeric-paper almost like a weak alkaline solution, for example, lime-water. If the coloration of turmeric-paper by boracic acid and alkaline solutions originated in a similar cause, an increased coloration must be produced by solution of borax. But the reaction of boracic acid upon turmeric-paper by a solution of borax occurs in a greatly heightened degree, when an acid, and especially a stronger acid, is added to it. It then indeed acquires a tint somewhat different from that produced by boracic acid, but it may be employed with great advantage in detecting even small quantities of boracic acid or of a borate in a solution.

Boracic acid is not the only acid which exhibits a peculiar behaviour towards turmeric-paper. Titanic acid, tantalic acid, the acids of niobium, stannic acid, and glucina, exhibit a similar behaviour when dissolved in strong acids, but most of the changes of the turmeric-paper produced by acids, are somewhat, although not very remarkably different from that caused by boracic acid.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 573.

On Angostura Bark and its Essential Oil. By Dr. C. Herzog.

Saladin found in Angostura bark an indifferent substance which he called Cusparine. The author has in vain endeavoured to prepare this body, which is said to be crystallizable. The author considers it possible that the preparation was unsuccessful in consequence of the difficulty of obtaining the solution which contains it in a colourless state. He found, however, that the bark contains a substance which is thrown down by caustic soda as a yellow precipitate from the extract purified by means of basic acetate of lead, freed from excess of the lead-salt by sulphuretted hydrogen, and further purified by animal charcoal; this precipitate, however, undergoes a change even on the filter, and becomes converted into a blackish-brown resinous body. By continued washing in water this dissolves with a cherry-red colour, but then again changes, and, like a vegetable chameleon, passes through all sorts of colours.

The author was more successful in the preparation of the volatile

oil of the bark. 4 pounds of coarsely pounded bark were submitted to distillation with the corresponding quantity of water; by this means $\frac{3}{4}$ per cent. of essential oil were obtained, consequently more than twice as much as has hitherto been ascribed to it. Its properties and elementary composition could therefore be more accurately studied.

It was impossible to distil the oil again in the presence of water, although when set free from the bark, it was carried over by the aqueous vapours. An addition of chloride of sodium gave no better result. The aqueous fluid was removed as much as possible by means of a siphon, and the oil was then left standing for about two days upon perfectly pure, dry chloride of calcium, and frequently shaken.

The oil poured away perfectly clear was then distilled with a thermometer immersed in it in a small glass retort by means of heated air, in the small distilling apparatus described by the author. At a temperature of 392° only a few drops passed over, although the author maintained the temperature for a long time at this point. It was only when the thermometer rose to 511° F. that a uniform ebullition took place, during which the oil passed without decomposition. The external thermometer, that is to say the one which did not sink into the fluid, showed 528° F. The residue in the retort was of a dark colour; the last portions that passed were collected separately.

The pure oil was of a pale wine-yellow colour, and possessed a peculiar aromatic odour, resembling that of lovage, and a taste which was at first mild, but afterwards somewhat acrid. Its spec. grav. was 0·934. Boiling-point 511° F., probably one of the highest boiling-points for an essential oil.

On the average of two concordant analyses, the oil consisted of—

C	79·60	13	79·59
H	12·31	12	12·24
O	8·09	1	8·17

If we suppose that most of the oxygenated oils also contain an oil free from oxygen of the formula $C^5 H^4$, the oxygenated oil would have the formula $C^8 H^8 O$, add to which that of the oil free from oxygen, $C^5 H^4$

$$= C^{13} H^{12} O.$$

Archiv der Pharm., cxliii. p. 146.

On Compounds of Hydrocarbons with Picric Acid.
By J. Fritzsche.

The author has found that picric acid is capable of combining with hydrocarbons.

Picric Acid and *Benzine.*—Pure benzine, freed as much as possible by repeated crystallization from foreign intermixtures, dissolves

picric acid in no inconsiderable quantity (8—10 per cent.) even at ordinary temperatures, but in far greater proportion with the assistance of heat, and for this reason the cooling of a solution saturated at a boiling heat furnishes an abundant crystallization, which, however, does not consist of pure picric acid, but of a compound of this with benzine. This compound forms shining, pale yellow, rhombic crystals, which are and continue perfectly transparent as long as they remain in the mother-liquor or in the atmosphere saturated with benzine, but on exposure to the air begin immediately to undergo change by the evaporation of benzine. First of all whitish-yellow, dull spots are produced upon the crystals; but these soon spread over the whole surface, and gradually penetrate more deeply into the crystals, until at length, the latter, still retaining their form, lose all their benzine, and there remains nothing but an aggregation of small crystals of picric acid, separable by a gentle pressure.

The compound of benzine with picric acid fuses at a high temperature to form a clear fluid of a pale yellow colour. Alcohol and æther dissolve the compound, but do not extract, as the author anticipated, the benzine contained in them, which is much more soluble than picric acid; the crystals retain their transparency in these solvents. The compound cannot be recrystallized from them. Even at ordinary temperatures water dissolves from the compound an amount of picric acid corresponding with its degree of solubility, and separates benzine; when boiled, it decomposes the compound completely, the benzine being volatilized with the aqueous vapours. Analysis gave—

Benzine.....	25·406
Picric acid.....	74·594

Picric Acid and *Naphthaline.*—The compound of naphthaline and picric acid is very easily obtained when the two substances are dissolved in alcohol with the aid of heat, and the solution is allowed to cool; it separates in golden-yellow needles, which may be washed upon a filter with a little alcohol and dried in the air after gentle pressure between bibulous paper, without any fear of decomposition. If cold, saturated alcoholic solutions of picric acid and naphthaline be brought together, the compound also separates, but in far finer crystals than from the hot solution. Benzine may also be made use of as a solvent for the preparation of the compound.

The golden-yellow crystals of the compound of naphthaline with picric acid fuse at 300° F. to form a clear fluid of a deep orange-yellow colour; no trace of moisture or of any other fluid body is driven off, and only a little naphthaline is volatilized. Alcohol, æther, and benzine dissolve the compound unchanged, and on evaporation it separates again without alteration; water at the ordinary temperature, on the contrary, extracts picric acid from the surface of the crystals. On boiling with water naphthaline is volatilized, the compound being slowly decomposed, but a portion of the naphthaline dissolves at the same time in the solution of picric acid, and when the solution is filtered whilst boiling, it deposits on cooling

fine microscopic needles of the compound of naphthaline and picric acid, which is consequently slightly soluble in water. Analysis:—

Naphthaline.....	35·85
Picric acid	64·40

Picric Acid and *the Hydrocarbon*, $C^{28}H^{10}$.—The author prepared this hydrocarbon from the heavy oils of coal-tar, manufactured by Kurtz, Cropper and Co. He dissolved it in benzine, and brought it in contact with picric acid. After boiling with an excess of picric acid, deep ruby-red, rectangular, and probably quadratic prisms separated on cooling.

Both alcohol and æther have a decomposing action upon this compound, from their dissolving picric acid far more readily than the hydrocarbon, so that they extract the former, but leave the latter for the most part undissolved; with alcohol the picric acid may be entirely extracted. Water, even at ordinary temperatures, extracts picric acid from the surface of the crystals of the compound; this appears both from the yellowish colour which the water acquires, and from the whitish stratum of hydrocarbon which is gradually formed upon the surface of the crystals in consequence of this property; when the temperature is raised this action is far more considerable, but attains its limit as soon as the stratum of hydrocarbon becomes impenetrable. The melting-point of the compound was found by the author to be about 338° F., by heating it in the oil-bath in a test-tube, and repeatedly observing the temperature of the oil-bath, both at its fusion and solidification; that of the hydrocarbon is about 410° F., a difference which is explained by the melting-point of picric acid, 248°—257° F., observed under the same conditions.

Analysis gave—

58·94 Carbon, and 3·14 Hydrogen; *i. e.*

C	58·94	12+28	=	3000·00	58·97
H	3·14	8 10		162·50	3·19
N		3		525·18	10·32
O		14		1400·00	27·52

In its properties the hydrocarbon, $C^{28}H^{10}$, agrees most closely with Laurent's *pyrene*, but differs essentially therefrom both in its composition, and still more in its far higher melting-point. But it also possesses some similarity with anthracene, and this relation can only be cleared up by a further careful study of all these bodies, to which the author proposed shortly to devote the considerable quantity of substance which he hoped to obtain from the materials above mentioned.

In conclusion, the author also calls attention to a relation in which the hydrocarbon, $C^{28}H^{10}$, may be considered to stand with benzine and naphthaline; thus, if we take the formulæ—

$C^{12}H^{6}$
$C^{20}H^{8}$
$C^{28}H^{10}$

we find that naphthaline is distinguished from benzine by containing an additional $C^8 H^2$, and that when $C^8 H^2$ is added to the formula of naphthaline, we obtain that of the new hydrocarbon. If we now suppose the hydrocarbon $C^8 H^2$ to be contained in benzine, that substance might be expressed by the formula $C^4 H^4 + C^8 H^2$, naphthaline by the same formula with duplication, and the third hydrocarbon with triplication of the second member, thus:—

$$\begin{array}{llll} C^4 H^4 + & C^8 H^2 & = & C^{12} H^6 \\ C^4 H^4 & 2(C^8 H^2) & & C^{20} H^8 \\ C^4 H^4 & 3(C^8 H^2) & & C^{28} H^{10} \end{array}$$

The analysis of this hydrocarbon gave—

C	94·16	28	2100	94·38
H	5·74	10	125	5·62

Bull. de St. Pétersb., xvi. p. 150.

On Lactic Acid. *By* A. Brüning.

The author's object was to decide whether lactic acid written $C^{12} H^{12} O^{12}$ saturates 4 equivs. of base, or regarded as $C^6 H^6 O^6$, saturates 2 equivs. of base.

The lactic acid employed in the experiments was prepared by Bensch's process. From this the author always first prepared the zinc-salt, which was purified by recrystallization. For the solution of his problem he selected the following salts.

Protolactate of tin, prepared by mixing a solution of lactate of soda with one of protochloride of tin, has the composition $C^{12} H^8 O^8 + 4SnO$, not as stated by Engelhardt and Maddrell, $C^{12} H^{10} O^{10} + 4SnO$. Consequently 4 equivs. of hydrogen are actually displaced by SnO in the lactic acid.

With *peroxide of mercury* the author did not obtain a tetrabasic salt. When he saturated dilute boiling lactic acid with peroxide of mercury in accordance with the directions of Engelhardt and Maddrell, he observed a strong evolution of gas and an odour of aldehyde. The salt which separated by crystallization was a protosalt. This does not agree with the salt described by Engelhardt and Maddrell as the protosalt, but with the colourless salt, regarded as a persalt by those chemists. This salt is white, is not decomposed by boiling water, and loses no water at 212° F. Its analysis led to the formula of the bibasic protosalt, $C^{12} H^{10} Hg^4 O^{12}$.

By saturating lactic acid with hydrated oxide of bismuth, the author obtained a basic salt, which was mixed with the excess of oxide of bismuth added. The solution filtered therefrom, furnished on evaporation the monobasic bismuth-salt, $BiO^3 + C^{12} H^9 O^9$.

It appears therefore on the whole that lactic acid may take up 4 atoms of base, although these tetrabasic salts are not easily obtained.

By the action of perchloride of phosphorus upon lactic acid, which was for the most part converted into anhydride by heating to 266° F., the author did not obtain any simple result. Gaseous

protochloride of methyle was evolved without any application of heat; on heating the contents the retort became black, with evolution of much muriatic acid gas and oxide of carbon. The residue contained phosphoric acid and anhydride of lactic acid.

In the lactic fermentation, as is well known, other products, among which mannite and gum occur in abundance, are formed together with the lactic acid. The gum detected by Kirchhof has been obtained pure by the author in the following way. The aqueous solution of lactic acid produced in the process is strained away from the residue, the lime precipitated by sulphuric acid, and the aqueous solution by alcohol. The precipitate is repeatedly dissolved in water acidulated with muriatic acid, and purified by repeated precipitation by alcohol. When dried at 266° F. and analysed, it gave,—

C	44·44	12	43·61
H	6·17	10	6·25
O	49·39	10	50·14

The gum produced in the fermentation is not identical either with dextrine or arabine. In its alkaline solution it does not reduce peroxide of copper, but a pale blue precipitate is formed which does not change its colour by boiling; in this respect it resembles arabine. On the other hand, the aqueous solution deviates the plane of polarization to the right like dextrine. No mucic acid is produced by treatment with nitric acid.—Liebig's *Annalen*, civ. p. 191.

On Compounds of Vanadium with Nitrogen. By E. URLAUB.

The author has prepared compounds of vanadium, similar to those of molybdenum recently described by him.

Vanadinnitride.—If ammonio-perchloride of vanadium be heated in a glass tube, whilst dry ammonia free from air is passing through, the bodies are decomposed, muriate of ammonia is evolved with some ammonio-perchloride of vanadium. There remains a black mass, which is brilliant at some points, when it lies close to the glass.

It is washed with water containing ammonia, and dried *in vacuo* over sulphuric acid. The reaction of nitrogen is obtained with hydrate of potash during fusion, and with hypochlorite of soda. The product contains 15·531—15·773 per cent. of nitrogen and 0·104 per cent. of hydrogen. The formula VaN requires 16·964 nitrogen. If the small quantity of hydrogen be disregarded, the calculation from the above formula perhaps agrees closely enough with the results obtained.

A product prepared at a high temperature consisted of $VaN + 3Va^2N$, according to analysis; it therefore contained bivanadinnitride as well as vanadinnitride.

Bivanadinnitride, Va^2N, is formed by the same process when the glass tube is heated to slight redness. It has a silvery lustre

when it is in contact with the glass, is black in the interior, and gave 90·520 of vanadium and 9·48 of nitrogen.

Trivanadinnitride, $Va^3 N$, is obtained, when ammonio-perchloride of vanadium is exposed in a Bohemian glass tube to a strong red heat while ammonia is flowing through. The product contains 6·427 of nitrogen.

If these nitrides be exposed to a white heat in a porcelain tube, vanadium is obtained in the metallic form, which furnishes no ammonia when fused with hydrate of potash.

Vanadic acid also furnishes nitrogenous compounds when ignited in ammonia; these yield some water, both when burnt in oxygen and when ignited in hydrogen. The products obtained at higher temperatures contained no hydrogen, and no oxygen could be detected by ignition in hydrogen; this is probably to be ascribed to these products containing suboxide.—Poggendorff's *Annalen*, ciii. p. 134.

Notice of a new Base containing Osmium and the Elements of Ammonia. *By* Wolcott Gibbs *and* F. A. Genth.

An investigation of the ammonia-cobalt bases, the results of which have appeared in this Journal, has led us to direct our attention to the production of similar compounds with other metals. We have in particular studied the action of the mixed oxides of nitrogen, NO^2, NO^3, and NO^4, upon ammoniacal solutions, and have obtained results which will form the subject of a future communication. In the course of an extended study of the platinum metals, for which we have enjoyed peculiar facilities, we have remarked that osmium forms with ammonia a well characterized base, all the salts of which appear to be highly crystalline.

The chloride of this base is a yellow crystalline salt, first obtained by Fremy in 1844, and described in his memoir* on the metallic acids, under the name of osmiamid. To this body Fremy attributes the formula $NH^4 Cl + Os O^2 . NH^2$, according to which it is to be viewed as a compound of chloride of ammonium with an amide of osmious acid.

We have, however, found that the substance in question is a true chloride which yields a beautiful salt with bichloride of platinum, and which by double decomposition with salts of silver enables us to form a well-defined sulphate, nitrate, oxalate, &c. The best method of forming these salts, however, is precisely that which Fremy employed for the chloride, and consists in adding a solution of osmite of potash to a cold solution of an ammoniacal salt, when the new salt is immediately formed and crystallizes from the solution.

The salts of the new base have a very beautiful orange-yellow colour. They are nearly insoluble in cold water; hot water dissolves them more readily, but the solutions are easily decomposed with evolution of osmic acid. We are not as yet prepared to pronounce

* Annales de Chimie et de Physique, 3d series, vol. xii. p. 521.

with certainty upon the constitution of these salts, the analyses being difficult and tedious. We may, however, remark that Fremy's analysis of the chloride appears to be correct, and that we attribute to it the rational formula

$$2NH^3 \frown Os\,O^2, Cl,$$

according to which the base will be uniacid. The results of our complete investigation will form the subject of another communication. Iridium and rhodium form with ammonia and deutoxide of nitrogen bases analogous to xanthocobalt, with the study of which we are also occupied.—Silliman's *Journal* for March, 1858.

Testing of Sulphuric Acid for Nitric and Hyponitric Acids. *By* A. Vincent.

Some iron-filings are thrown into a few grammes of the sulphuric acid to be tested; if nitric or hyponitric acids be present, the colour produced is rose-red, bluish-red, or violet-blue, according to the degree of purity.—*Journal de Chimie Méd.* 1857, p. 522.

On the Diffusion of Fluorine. *By* J. Nicklès.

The author finds fluorine in the blood, in the urine, and in the bones. 10 grms. of the lime salts of the bones contain, according to Berzelius, 3 grms. of fluoride of calcium; the author regards this number as far too high, according to his determinations the amount is scarcely 5 centigrms. of fluoride of calcium in 1 kilogrm. of the substance of the bones.

The animal organism acquires fluorine,—1st, by drinking water, and 2nd, by vegetables.

Mineral waters contain fluorine in abundance as compared with drinking-waters, and the author is of opinion that the efficacy of mineral waters may be explained from this circumstance. The water of the Seine at Paris, and the water of the Rhine at Strasburg contain the least fluorine. Of the French waters one of the richest in fluorine is that of the Somme at Amiens. The richest met with by the author are the waters of Contrexéville, Antogast, and Châtenois. One litre of these waters was sufficient for the undoubted recognition of the fluorine. The water of the Atlantic Ocean contains extremely little fluorine. 300 litres of it are scarcely sufficient for the detection of fluorine.

As regards the diffusion of fluorine in the crust of the earth, fluoride of calcium occurs in all waters which contain carbonate of lime. All sedimentary rock formations may contain fluorine.

To detect the fluorine, the fluorine set free must be allowed to act upon a plate of rock-crystal instead of glass. The sulphuric acid by means of which the fluorine is set free, must be free from hydrofluoric acid. To obtain such acid, ordinary concentrated sulphuric acid is mixed with a little water, and placed for a long time in a place where it becomes heated to 302°—356° F.

As a solvent muriatic acid is employed, because this occurs in commerce free from fluorine; sulphuric acid must never be employed for determinations of fluorine. At any rate fluorine has often been found where none exists, because sulphuric acid always contains fluorine.—*Comptes Rendus*, xlv. p. 331.

On the Combination of Nitrate of Soda with Nitrate of Silver. By H. Rose.

It has long been known that several salts of soda have the same form as the corresponding salts of silver. It is remarkable, however, that nitrate of soda is not isomorphous with nitrate of silver, although, as is well known, both may easily be prepared in very distinct crystals in the anhydrous state. Nitrate of silver may nevertheless be made to assume the rhombohedric form of the crystal of nitrate of soda, when the two salts are allowed to crystallize from a common solution.

If the solution contains an excess of nitrate of silver, and it is gradually evaporated over concentrated sulphuric acid, dimetric crystals of this salt, containing no soda, first of all separate. The subsequent crystallizations, however, have most distinctly the rhombohedral form of nitrate of soda, but contain besides this nitrate of silver, and this in very various proportions. Once the crystals were obtained of the composition $AgO + NO^5 + 2NaO, NO^5$; in other crystals 1 atom of nitrate of silver was combined with 3·18, 3·74, and 4·2 atoms of nitrate of soda, so that in these double compounds the two bases, oxide of silver and soda, may replace each other in indefinite proportions.—*Bericht der Akad. der Wiss. zu Berlin*, 1857, p. 474.

On the Constitution of Hyposulphuric Acid. By C. J. Koene.

The author regards hyposulphurous acid, the acid of Langlois, and that of Fordos and Gélis, as

SO^2, S, (oxysulphosulphuric acid of the author)
SO^3, SO^2 S
SO^3, SO^2 S^2.

The author compares the reactions which are peculiar to hyposulphuric acid, and concludes therefrom that it is a conjugate acid of the formula

$$HO + SO^3, SO^2.$$

Poggendorff's *Annalen*, ciii. p. 171.

On the Occurrence of Salicylate of Methyle in Monotropa Hypopitys. *By* Dr. F. L. Winkler.

The distillate of *Monotropa Hypopitys* with nearly developed flowers, furnishes an oil which is identical with the oil of wintergreen (from *Gaultheria procumbens*).—*Neues Jahrb. für Pharm.*, vii. p. 107.

THE CHEMICAL GAZETTE.

No. CCCLXXV.— June 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Origin of the Hippuric Acid in the Urine of the Herbivora. *By* Dr. W. HALLWACHS.

ROUELLE in 1773 discovered benzoic acid in the urine of herbivorous animals, and this discovery was afterwards confirmed by Fourcroy and Vauquelin. The latter came to the conclusion that benzoic acid must be contained in the food-plants of those animals. Giese found no benzoic acid in the plants, and therefore regarded it as a product of animalization. Wöhler subsequently observed the passage of benzoic acid unchanged through the organism, and therefore thought that its origin must be sought in the food-plants of the Herbivora; he supposed that the benzoic acid found by Vogel in *Melilotus* and *Anthoxanthum* might also occur in other meadow grasses.

When Liebig discovered that the substance found in the urine of the Herbivora and regarded as benzoic acid was not benzoic acid, but a distinct nitrogenous acid, to which he gave the name of *hippuric acid*, and on the other hand, Boutron-Charlard, Boullay, Delalande, and others showed that the crystallized body prepared from the above-mentioned plants was also not benzoic acid, but a substance identical with the stearoptene of Tonquin beans, which they called *cumarine*, it became evident either that the hippuric acid found in the urine must have some other origin, or that cumarine must be capable of effecting the formation of hippuric acid in the organism.

In 1842 Wöhler and Keller made an experiment on this subject. Keller took benzoic acid at night, and in the morning found hippuric acid in abundance in his urine. A nitrogenous body had attached itself to the non-nitrogenous benzoic acid, and the hippuric acid was separated as a soda-salt. Benzoic acid introduced into the organism reappears as hippuric acid. The urine of the Herbivora contains the latter in abundance; the question is, do the aliments of the animals, especially meadow grasses, contain benzoic acid or a benzoyle compound?

There is little difficulty in determining the presence or absence of benzoic acid, but the detection of other benzoyle compounds is not so easy. Regard must be had not only to the known compounds, but also to others which may not yet have been discovered. For the detection of the latter the behaviour of the known compounds must guide us to methods. Of these we know that some are decomposed by treatment with nitric acid, others by the action of chromic acid, by treatment with peroxide of manganese and sulphuric acid, or by boiling with baryta-water, &c., and that benzoic acid, or oil of bitter almonds, and sometimes both together, always occur as the products of their decomposition.

By treating the various grasses with different solvents, and exposing the residue obtained by evaporation to the above-described actions, any benzoyle compound that may be present must betray its existence by the production of benzoic acid or oil of bitter almonds. When the principal grasses, &c. had been collected and sorted, it had to be determined whether these grasses were adapted to the experiment in hand,—whether a cow after eating them would secrete any hippuric acid.

The urine of a cow fed upon grass and hay, amounted to 5080 cub. cent. in 24 hours. 1000 cub. cent. of this contained 9·5 grms. of hippuric acid, so that the cow secreted more than 50 grms. of hippuric acid in 24 hours. The same cow was then fed for four days with the selected hay and grasses, and produced 4400 cub. cent. of urine in the last 24 hours. 1000 cub. cent. of this urine contained 12·2 grms. of hippuric acid, so that the amount of this acid secreted was not essentially changed, and the hay might be employed without hesitation in the investigation.

All the plants, including *Anthoxanthum* and *Holcus*, were first tested for benzoic acid, the different species of the same genus being taken together; no benzoate, or free benzoic acid could be obtained either from the extract with lime-water or from the alcoholic extract.

In testing *Anthoxanthum* and *Holcus*, it appeared necessary to determine whether these plants contained only cumarine, or benzoic acid alone, or both together; the investigation showed that both plants contain cumarine, but not benzoic acid; the assumption that hippuric acid is formed from the benzoic acid contained in these plants, consequently falls to the ground.

Numerous experiments showed that cumarine when introduced into the organism is incapable of giving rise to the secretion of hippuric acid; it rather passes unaltered through the organism. In these experiments it was necessary to determine with certainty as to the presence or absence of small quantities of hippuric acid in the urine. The method employed differs in one respect from that described by Lehmann, in which the alcoholic extract of the evaporated urine is mixed with an excess of solution of oxalic acid during its evaporation. Oxalate of urea is insoluble in this fluid. If it be now evaporated and extracted with æther which contains $\frac{1}{6}$th of alcohol, a drop of the filtrate evaporated under the

microscope presents beautiful prismatic crystals which so strikingly resemble hippuric acid, that further examination is readily given up. The crystals obtained in many cases are, however, *oxalic acid*, which is by no means difficult of solution in æther and alcohol, whilst oxalate of urea is not taken up. To get rid of the dissolved oxalic acid, the residue of the evaporation of the ætherial extract was treated with lime, and the fluid filtered from the lime precipitate was concentrated and mixed with muriatic acid.

In testing for the benzoyle compounds, the method above referred to was followed. The extracts were treated with decomposing agents, and the products obtained tested for benzoic acid or oil of bitter almonds, as all benzoyle compounds furnish these bodies by the action of the agents employed.

The selected plants were macerated with water and then distilled; the residue was mixed with an emulsion of peeled sweet almonds, left in contact therewith for one night, and again distilled. No oil of bitter almonds could be detected in either the first or second distillate. The absence of pre-existent oil of bitter almonds and of amygdaline in the plants investigated was consequently proved.

Experiments on the behaviour of chlorophyll in the organism, showed that the amount of chlorophyll in plants does not cause the secretion of hippuric acid. The experiments with chlorophyll are indicated particularly, because from its relation to indigo, a connexion, although a distant one, with the benzoyle series is conceivable. The treatment of the plants with æther was not repeated with every species, as by the extractions with alcohol exactly the same bodies are obtained in solution. By æther alone, only chlorophyll in company with a wax-like body is obtained.

The plants were then (each kind by itself) completely exhausted, first with alcohol and then with water, and of each extract from 2—4 ounces were taken for each of the following treatments:—

1. With chromate of potash and sulphuric acid.
2. With peroxide of manganese and sulphuric acid.
3. With dilute nitric acid.
4. With dilute muriatic acid.
5. With caustic baryta.

In *none* of the experiments was any proof obtained of the formation of oil of bitter almonds or benzoic acid. It is not said that these bodies never made their appearance, on the contrary it must be admitted that they actually were produced both in the treatment with chromic acid and in the oxidation with peroxide of manganese and sulphuric acid, as the alcoholic and aqueous extracts contained proteine substances, and these furnish the above-mentioned bodies, with others, under the influence of oxidizing agents.

The detection of *small* quantities of benzoic acid or oil of bitter almonds could not decide the question on this very account. If a peculiar benzoyle compound were present, it must have betrayed its existence by the production of considerable amounts of its characteristic products of decomposition.

The results of the investigation may be formulated as follows:—

1. No benzoic acid is contained in the plants examined, after eating which a cow secreted hippuric acid in abundance.

2. The plants contain no benzoyle compound, which may be decomposed in the organism, furnishing benzoic acid or oil of bitter almonds, and thus give rise to the secretion of hippuric acid.

3. Cumarine, formerly regarded as benzoic acid, and

4. Chlorophyll, which may be considered to be allied to the benzoyle series, pass unchanged through the organism.—Liebig's *Annalen*, February 1858, p. 207.

On the Action of Sulphurous Acid and the Sulphites upon Sesquioxides of Aminocobalt. By Dr. CARL KÜNZEL.

The author first proves that sesquichloride of pentaminocobalt has not Claudet's formula $Co^2 Cl^3 N^5 H^{16}$, but tha tassumed for it by other chemists, $Co^2 Cl^3 N^5 H^{15}$. By treating this compound with sulphite of ammonia he obtained

Sulphite of the Sesquioxide of Triaminocobalt, $Co^2 O^3, 3NH^3 + 3SO^2 + HO$.—It is produced when the solution of sesquichloride of pentaminocobalt in water, to which a little ammonia is added, is mixed with so much sulphite of ammonia that the fluid no longer smells either of sulphurous acid or of ammonia. The solution, which is originally red, acquires a dark yellow colour and yellow acicular crystals of sesquisulphite of triaminocobalt separate; these are removed from the fluid and washed with water. According to the concentration and temperature of the fluids, the sesquisulphite is obtained either in the form of a yellow powder consisting of microscopic acicular crystals, or in larger needles of great lustre and considerable hardness. The compound is insoluble in cold water; by long boiling with water it is slowly decomposed; when heated in a glass tube it furnishes water, ammonia, and sulphite and sulphate of ammonia, whilst protosulphate and persulphate of cobalt remain.

Ammonia has no action upon it in the cold; by long boiling it is decomposed with formation of a yellow solution. Muriatic acid effects a slow decomposition in the cold, and a more rapid one at a boiling heat; sulphurous acid is evolved. Dilute sulphuric acid behaves like muriatic acid. Concentrated sulphuric acid decomposes the salt with evolution of sulphurous acid. Solution of potash at a boiling heat, causes evolution of ammonia and deposition of oxide of cobalt. Analysis:—

Co	24·67	2	24·103
S	20·096	3	20·123
N	17·37	3	17·363
H	4·184	10	4·274
O	33·49	10	34·137

This compound is produced in accordance with the equation—

$$Co^2 Cl^3 + 5NH^3 + NH^3 + 3HO + 3(NH^4 O + 2SO^2) = (Co^2 O^3 + 3NH^3 + 3SO^2 + HO) + 3(NH^3 HCl) + 3(NH^3 . HO + SO^2).$$

Sulphite of the Sesquioxide of Pentaminocobalt, $2Co^2O^3+5NH^3+6SO^2+9HO$.—To obtain this, a current of sulphurous acid is conducted through a solution of sesquichloride of pentaminocobalt in ammonia; the red solution first becomes yellow, then brownish-red, and the compound then separates as a brown, heavy, granular-amorphous precipitate. Or finely powdered sesquisulphite of triaminocobalt is suspended, and sulphurous acid passed through it for a long time.

From the mother-liquor of this salt, which smells strongly of sulphurous acid, sesquisulphite of triaminocobalt separates in beautifully developed crystals, when ammonia is added to neutralization.

Sesquisulphite of pentaminocobalt is insoluble in cold water; when boiled with water it is slowly decomposed, and sulphuric acid may be detected in the solution obtained. Muriatic acid effects a slow decomposition in the cold; when boiled, it causes decomposition with evolution of sulphurous acid. Dilute sulphuric acid behaves like muriatic acid. Concentrated sulphuric acid decomposes the compound immediately, with evolution of sulphurous acid. Concentrated nitric acid evolves nitrous acid with it. Solution of potash dissolves the compound in the cold, forming at first a brown fluid, from which a brown precipitate soon settles with evolution of ammonia; boiling solution of potash separates oxide of cobalt with evolution of ammonia. Ammonia, when boiled, gives a yellow solution, probably $Co^2O^3+5NH^3+3SO^2$, and a yellow crystalline precipitate, $Co^2O^3+3NH^3+3SO^2$. Analysis:—

Co	22·51	4	= 118·0	22·296
N	13·36	5	70·0	13·743
S	18·32	6	96·0	18·448
H	4·59	24	24·0	4·576
O	41·22	27	216·0	40·937

Sulphite of the Sesquioxide of Biaminocobalt, $Co^2O^3+2NH^3+3SO^2+5HO$, was obtained when the solution of sesquichloride of pentaminocobalt in water, to which a very little ammonia was added, was somewhat supersaturated with bisulphite of ammonia, and the dark brown solution left standing for a long time. Brown octahedra are produced, which are almost insoluble in water, and evolve sulphurous acid with sulphuric acid. Solution of potash sets free no ammonia in the cold, but a large quantity when heated, whilst a blackish-brown precipitate is thrown down. Ammonia, when boiled, gives a yellow solution, and a yellow precipitate remains, but this dissolves almost without residue in a great quantity of ammonia. When heated in a glass tube, water, ammonia, and sulphate of ammonia are evolved, and protosulphate of cobalt remains. Analysis:—

Co	11·87	2	= 59	23·185
N	10·855	2	28	10·822
S	18·600	3	48	19·337
H	4·264	11	11	4·325
O	43·411	14	112	42·331

Hyposulphate of the Sesquioxide of Tetraminocobalt, Co^2O^3+

$4NH^3+2S^2O^5$, is obtained when the solution of sesquichloride of pentaminocobalt in much ammonia is mixed with only so much sulphurous acid that a great excess of free ammonia still remains in the fluid. A dark yellow fluid is obtained, which, when exposed to the air in a loosely stoppered bottle, deposits brownish-yellow or yellow crystals. If the concentrated yellow fluid be exposed in shallow vessels immediately after the passage of the sulphurous acid to the strong action of the air, or if it be brought repeatedly in contact with the air by frequent pouring from one vessel into another, it rapidly becomes turbid by the deposition of a yellow indistinctly crystalline paste. The crystalline products thus obtained are of very variable composition; they all contain an oxide of sulphur, ammonia, oxide of cobalt, and also chlorine in variable quantities.

On the other hand, the author obtained a salt of constant composition when he dissolved these chlorinated products in a mixture of ammonia and alcohol; from this solution it shoots out in crystals on cooling. It is washed with alcohol and dried *in vacuo*. It appears as a crystalline mixture of very light, fine lamellæ of a yellow colour and silky lustre, amongst which, however, no distinctly developed crystals are to be detected even under the microscope. In water and dilute alcohol, the crystals are soluble with a yellow colour; boiling water decomposes them, as does the action of the air upon the solution and upon the dry crystals. Dilute sulphuric acid does not set free sulphurous acid, but this is evolved by concentrated sulphuric acid. Chloride of barium produces no precipitate either in the aqueous solution, or in the solution acidified with muriatic acid; but if the solution be boiled with nitric acid, sulphate of baryta is thrown down. Solution of potash at first gives no precipitate in the cold; by long standing and by the application of heat, brown oxide of cobalt is thrown down with evolution of ammonia. When the compound is heated in a glass tube, ammonia and sulphate of ammonia are evolved, and oxide and protosulphate of cobalt remain. Analysis:—

Cobalt	20·00	2=	59	19·783
Sulphur	21·69	4	64	21·476
Ammonia	23·06	4	68	22·900
Oxygen	35·25	13	104	35·841

Basic Sesquinitrate of Pentaminocobalt, $2(Co^2O^3+5NH^3)+5NO^5$, is obtained when a solution of nitrate of cobalt in ammonia is exposed to the air until it has acquired a dark olive-brown colour, so that Fremy's oxycobaltia is contained in it, and mixed with a solution of nitrate of ammonia; the brown colour of the fluid soon passes into an intense yellow, and a yellow, crystalline, very loose precipitate separates. This is difficult of solution in cold, but dissolves with ease in hot water; in boiling water it is slowly decomposed; cold concentrated nitric acid dissolves it; concentrated sulphuric acid, when strongly heated, gives nitrous acid, whilst the fluid acquires an intense purple-red colour. Potash evolves ammonia, and throws down brown oxide. When heated in

a glass tube or on platinum-foil, the compound melts, and becomes decomposed with a brisk detonation. Analysis:—

Cobalt	19·47	24	= 118	19·50
Nitrogen	11·551	5	70	11·690
Ammonia	28·053	10	170	26·766
Oxygen	40·924	31	248	40·984

The production and composition of this compound confirm Fremy's statements as to the composition of the oxycobaltias, upon which doubts have lately been thrown. Admitting the formulæ of these, the production of this nitrate is explained as follows:—

$$2(Co^3O^4 + 5NH^3 + 2NO^5) + NO^5 = 2(Co^3O^3 + 5NH^3) + 5NO^5.$$

Journal für Prakt. Chemie, lxxii. p. 209.

On some of the Products of the Destructive Distillation of Boghead Coal.—Part I. *By* C. Greville Williams, *Lecturer on Chemistry in the Normal College, Swansea.*

[Concluded from page 190.]

Butyle.—The following experiments were the first made with the radicals from Boghead naphtha, but are placed here in their proper sequence with regard to the other homologues.

It has been found that the separation of the hydrocarbons can be effected by other means than those adopted for the preparation of the radicals; the details of the method belong to a series of experiments to be given in Part II. It is to be understood, therefore, that the nitric acid process was adhered to for the isolation of the bodies described in this paper.

After preparation of the butyle, I proceed to determine the vapour-density of the fractions, the results being embodied in the annexed Table.

Vapour-densities of fractions from 104° *to* 129°, *after treatment with nitric acid, &c.*

Boiling-point.	Excess of weight of balloon.	Temperature of vapour.	Temperature of air.	Pressure.	Capacity of balloon.	Residual air.	Density.
	grm.			mm.	cub. cent.	cub. cent.	
104° to 107°	·5332	154°	19°	752	298·5	·5	3·63
104 to 110	·4365	171	16	752	268·0	5·0	3·66
107 to 110	·5030	163	16	761	281·5	1·5	3·73
110 to 116	·4950	173	16	761	277·5	2·0	3·82
121 to 127	·5489	179	18	760	274·5	0·0	4·11
126 to 129	·5545	160	14	750	268·5	2·3	4·09

It was evident from the foregoing determinations, that the boiling-point of the hydrocarbon having the formula $C^{16}H^{18}$ was between 116° and 121°, but this being higher than was anticipated, it appeared

probable that the fractions used had not been treated sufficiently with nitric acid: a portion of somewhat lower boiling-point than those in the Table was therefore repeatedly acted on until the impurity was entirely removed, and the separated acid, on being diluted with water, yielded not the slightest milkiness. The annexed were the results obtained with the hydrocarbon so purified:—

	Portion distilling, 100° to 101°.	Portion distilling, 101° to 103°.
Temperature of air	17°	17°
Temperature of vapour	145°	148°
Pressure	776·2 mm.	776·2 mm.
Excess of weight of balloon..	·5545 grm.	·5305 grm.
Capacity of balloon	308 cub. cent.	295 cub. cent.
Residual air	4·5 cub. cent.	5·0 cub. cent.
Density of vapour	3·63	3·66

The repeated treatment with nitric acid, although it had the effect of raising the density, did it to so slight a degree, that it was clear the boiling-point of butyle from the Torbane-hill mineral was much higher than that found by other observers, and lay between 116° and 121°. Analysis gave the numbers annexed:—

	Calculation.		Experiment.			
			I.	II.	III.	IV.
C	16=96	84·2	84·1	84·2	84·0	83·9
H	18 18	15·8	15·7	..	15·7	15·9

The fourth analysis was made upon a different preparation to the others.

Kolbe's radical obtained by the electrolysis of butyric acid gave him the following numbers, which are sensibly the same as the above:—

	Kolbe.	
Carbon	84·1	84·0
Hydrogen.....	15·9	15·8

Annexed is a determination of the vapour-density of the fraction distilling between 116° and 121°.

Excess of weight of balloon..	·5270 grm.
Temperature of vapour	167°
Temperature of air	16°
Pressure.....	753 mm.
Capacity of balloon	280 cub. cent.
Residual air	1·0 cub. cent.

The formula $C^{16}H^{18}$ requires—

16 volumes carbon vapour.... 0·8290 . 16 = 13·264
36 volumes hydrogen..... 0·0692 . 36 = 2·491

$$\frac{15·755}{4} = 3·9387$$

Experiment.	Kolbe.	Wurtz.	Theory = 4 vols.
3·883	4·053	4·070	3·9387

Although the above numbers are exceedingly near those required by theory, it follows that the boiling-point of the hydrocarbon having the same formula as butyle from Boghead coal, is decidedly higher than that found by Kolbe and Wurtz. The boiling-point of Kolbe's hydrocarbon, obtained by electrolysis of valerianic acid, was 108°, and that of butyle, obtained by Wurtz by cohobating iodide of butyle over sodium, was 106°, whereas my hydrocarbon distilled in the sixteenth rectification between 116° and 121°. It will be seen that in the first and third analysis there is a tendency towards a deficiency in the hydrogen; on searching into the cause of this, it was found that a trace of one of the homologues of olefiant gas, to be described in the second part of this paper, remained in the fluid. This arose from insufficient treatment with nitric acid. The fourth analysis was made on a perfectly pure product. The results obtained further on with the other radicals are perfectly in accordance with those of other chemists. The density of the butyle, as analysed, was found to be 0·6945 at 18°, agreeing perfectly with Kolbe's determination made at the same temperature, which gave 0·6940. It undergoes considerable expansion with even a small rise of temperature, for Wurtz found the density at 0° to be 0·7057.

Amyle.—The experiments previously made having indicated somewhat too high a boiling-point for the butyle, it was considered necessary to examine the fractions having boiling-points at all approaching to that of amyle with great care, in order to ascertain whether the same difference would be found. The following Table contains the results:—

Vapour-densities of fractions from 154° *to* 169°, *after treatment with nitric acid, &c.*

Boiling-point.	Excess of weight of balloon.	Temperature of vapour.	Temperature of air.	Pressure.	Capacity of balloon.	Residual air.	Density.
	grm.			mm.	cub. cent.	cub. cent.	
154° to 160°	·6187	210°	19°	756	274	4·0	4·82
160 to 162	·7581	208	21	765·5	305·5	0	5·02
160 to 165	·7855	193	19	752	305·5	1·5	5·02*
163 to 164	·7518	210	20	765·5	298	0	5·11
166 to 169	·6980	207	18	757	275	0	5·11†

It was quite obvious, from the numbers condensed into the above Table, that the amyle from the Torbane-hill mineral boiled between 154° and 160°; but the first experiment which was made upon the entire fluid boiling between these points proving too low, a fraction

* From fraction of crude naphtha distilling between 154° and 160°.

† This resullt was obtained during the preliminary experiments the fluid had not been absolutely freed from bodies of lower boiling-point.

was selected distilling in the sixteenth rectification between 157° and 160°.

The following are the results, together with those obtained by Frankland and Wurtz:—

	Calculation.		Experiment.	Frankland.			Wurtz.
C^{20}	120	84·5	84·4	84·2	84·6	..	84·2
H^{22}	22	15·5	15·7	15·4	15·2	15·4	15·7

To confirm the result obtained in the analysis of the amyle from the above fraction, the density of its vapour was ascertained.

Excess of weight of balloon ..	·6746 grm.
Temperature of vapour	212°
Temperature of air.....	21°
Pressure	767·3 mm.
Capacity of balloon	283·5 cub. cent.
Residual air	·5 cub. cent.

The formula $C^{20}H^{22}$ requires—

20 volumes carbon vapour....	0·8290 . 20	= 16·580
44 volumes hydrogen.....	0·0692 . 44	3·045
		19·625

$$\frac{19{\cdot}625}{4} = 4{\cdot}906$$

Experiment.	Frankland.	Wurtz.	Theory.
4·930	4·899	4·956	4·906

The boiling-point of amyle, according to the most recent experiments on the subject*, is 158°, which agrees quite as nearly as could be expected with the above result. The density of the fluid was found to be (at 18°) 0·7365. Frankland found it 0·7704 at 11°, and Wurtz 0·7413 at 0°.

When Boghead amyle is cohobated with monohydrated nitric acid for some days, a large quantity of a nitro-acid is formed, which yields a silver salt of very sparing solubility. This acid will be described in a future communication, it being my intention to compare the products of the action of oxidizing agents on the radical from the Torbane-hill distillate, with those from amyle prepared by the action of sodium on the iodide.

Caproyle.—This radical was first isolated by Messrs. Brazier and Gossleth† in the course of their researches on caproic and œnanthylic acids; they obtained it by the electrolysis of œnanthylate of potash. Remembering that, as obtained by them, it had a boiling-point of 202°, I commenced in searching for it by taking the vapour-densities of the fractions a little above and below that point, and obtained the numbers annexed:—

* Wurtz, Ann. de Chimie et de Phys, 2me série, tome xliv. p. 292.

† Quarterly Journal of the Chemical Society, vol. iii. p. 226.

	Boiling-point, 196° to 199°.	Boiling-point, 202° to 208°.
Excess of weight of balloon..	·8855 grm.	·6680 grm.
Temperature of vapour	230°	233°
Temperature of air	15°	14°
Pressure	739·4 mm.	760·2 mm.
Capacity of balloon	322·5 cub. cent.	225 cub. cent.
Residual air	4·0 cub. cent.	·5 cub. cent.
Density.....	5·74	6·03

The hydrocarbon from the Boghead naphtha, of which I was in search, boiled therefore between 199° and 202°. The following are the results of analysis obtained by me and other observers in a combustion of the fluid distilling at that temperature:—

	Calculation.		Experiment.	Brazier and Gossleth.		Wurtz.
C^{24}	144	84·7	84·6	84·49	84·54	84·25
H^{26}	26	15·3	15·8	15·60	15·44	15·49

A determination of the vapour-density proved that the fraction boiling at 202° had not only the per-centage composition, but exactly the same condensation as the radical caproyle, thus:—

Excess of weight of balloon..	·8021 grm.
Temperature of vapour	231°
Temperature of air	15°
Pressure	739·4 mm.
Capacity of balloon	283·0 cub. cent.
Residual air	1·0 cub. cent.
Density.....	5·83

The formula $C^{24}H^{26}$ requires—

24 volumes carbon vapour....	0·8290 . 24	= 19·896
52 volumes hydrogen.....	0·0692 · 52	3·598
		23·494

$$\frac{23\cdot494}{4} = 5\cdot8735$$

Experiment.	Wurtz.	Theory.
5·83	5·983	5·8735.

It was found that as the radicals of higher boiling-point were reached, greater difficulty existed in getting rid of the last traces of nitrocompound: although repeatedly washed with monohydrated nitric acid to remove any that might remain in solution, and then with strong potash, the radical so obtained did not, at first, distil perfectly colourless, and, moreover, retained a slight odour of the nitrocompound. The fluid in this condition left a yellow residue on distillation. A few rectifications over sodium entirely removed the impurity, and the radical as analysed above was perfectly colourless and almost inodorous. Its density at 18° was 0·7568. Wurtz found it at 0° 0·7574. Messrs. Brazier and Gossleth do not state the density of the caproyle analysed by them.

It is submitted that the foregoing experiments prove that the distillate from the Torbane-hill mineral contains, in addition to

several other substances, a series of hydrocarbons having the percentage composition, density in the fluid and gaseous states, and also the boiling-point of the alcohol radicals. It is perhaps to be regretted that in investigating these bodies, we are unable to avail ourselves of active affinities of a kind tending to yield easily procured and definite compounds, the study of which would remove all doubt as to identity. It is also peculiarly unfortunate that the boiling-points of simple and compound radicals, as at present determined, show no fixed law; in fact, if we examine the only data in our possession on the subject, namely, the numbers given by Wurtz, we find no less than nine different values for the increment of $C^2 H^2$, as may be seen from the following Tables:—

I.	Boiling-point.
Ethylamyle $C^{14} H^{16}$	88°
Ethylbutyle $C^{12} H^{14}$	62°
Difference for $C^2 H^2$	26°

II.	Boiling-point.
Methylcaproyle $C^{14} H^{16}$	82°
Ethylbutyle $C^{12} H^{14}$	62°
Difference for $C^2 H^2$	20°

III.	
Butyle $C^{16} H^{18}$	106°
Ethylamyle $C^{14} H^{16}$	88°
Difference for $C^2 H^2$	18°

IV.	
Butyle $C^{16} H^{18}$	106°
Ethylbutyle $C^{12} H^{14}$	62°
2)	44°
Difference for $C^2 H^2$	22°

V.	
Butyle $C^{16} H^{18}$	106°
Methylcaproyle $C^{14} H^{16}$	82°
Difference for $C^2 H^2$	24°

VI.	
Butylamyle $C^{18} H^{20}$	132°
Butyle $C^{16} H^{18}$	106°
Difference for $C^2 H^2$	26°

VII.	
Butylamyle $C^{18} H^{20}$	132°
Ethylamyle $C^{14} H^{16}$	88°
2)	44°
Difference for $C^2 H^2$	22°

VIII.	
Butylamyle $C^{18} H^{20}$	132°
Methylcaproyle $C^{14} H^{16}$	82°
2)	50°
Difference for $C^2 H^2$	25°

IX.	
Amyle $C^{20} H^{22}$	158°
Butylamyle $C^{18} H^{20}$	132°
Difference for $C^2 H^2$	26°

X.	
Butylcaproyle $C^{20} H^{22}$	155°
Butylamyle $C^{18} H^{20}$	132°
Difference for $C^2 H^2$	23°

XI.	
Butylcaproyle $C^{20} H^{22}$	155°
Butyle $C^{16} H^{18}$	106°
2)	49°
Difference for $C^2 H^2$	24°·5

XII.	
Amyle $C^{20} H^{22}$	158°
Butyle $C^{16} H^{18}$	106°
2)	52°
Difference for $C^2 H^2$	26°

XIII.	
Caproyle $C^{24} H^{26}$	202°
Butylcaproyle $C^{20} H^{22}$	155°
2)	47°
Difference for $C^2 H^2$	23°·5

XIV.	
Caproyle $C^{24} H^{26}$	202°
Amyle $C^{20} H^{22}$	158°
2)	44°
Difference for $C^2 H^2$	22°

The following nine values are therefore obtained as the differences for C^2H^2; the Roman numerals indicate the number of the Table:—

III.	II.	IV., VII. and XIV.	X.	XIII.
18°	20°	22°	23°	23°·5

V.	XI.	VIII.	I., VI., IX. and XII.
24°	24°·5	25°	26°

Several curious facts become apparent from inspection of these numbers, not the least of which is, that, contrary to what has been found to hold with organic bases, isomeric radicals have the same, or nearly the same boiling-points, thus:—

Ethylbutyle=$C^{12}H^{14}$.	Propyle=$C^{12}H^{14}$.
Boiling-point.	Boiling-point.
62°	65°
Ethylamyle=$C^{14}H^{16}$.	Methylcaproyle=$C^{14}H^{16}$.
Boiling-point.	Boiling-point.
88°	82°
Amyle=$C^{20}H^{22}$.	Butylcaproyle=$C^{20}H^{22}$.
Boiling-point.	Boiling-point.
158°	155°.

If we consider the great difficulty of obtaining the radicals absolutely pure, we cannot be surprised at the fact that these numbers do not exactly accord.

It is not unworthy of note, that the great difference in the boiling-points of propyle and butyle from Boghead naphtha, which might have been urged as evidence against the view I have taken of their constitution, is, in fact, strong proof of the correctness of it, for the amount of that difference is 53° or 26° for C^2H^2, which happens to be the number occurring most frequently with the simple and compound radicals, and, moreover, it causes the Boghead propyle to have almost exactly the boiling-point of its isomer, ethylbutyle.

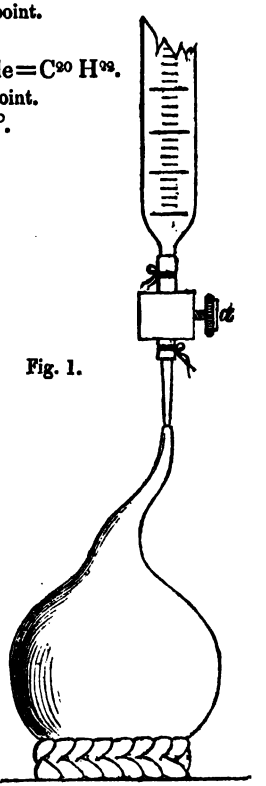


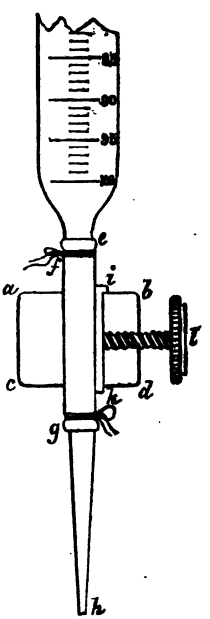
Fig. 1.

With regard to the fact of isomeric bases differing in boiling-point while isomeric radicals appear not to do so, it remains to be seen how much in the former case the variations are caused by difference of type.

In making the vapour-density determinations, I have endeavoured to find a method of shortening the time required for the performance of

some of the operations. One of the points to which I turned my attention was, to avoid the necessity of filling the balloon a second time with mercury or water in order to determine the residual air. For this purpose, as soon as the point of the balloon has been broken off under mercury and the latter has entered the globe, it is to be placed on a straw ring beneath a burette filled with the metal, as in fig. 1. The tube is divided into cubic centimetres and fractions. Having so adjusted the position of the balloon that the fine tube from the burette just enters the neck, the screw *a* is turned sufficiently to allow a slow stream of metal to flow until the condensed fluid exactly arrives at the opening, the altered level in the burette is then read off. It is evident that the difference between the first and second readings indicates a quantity of mercury exactly equal in volume to the residual air. The condensed fluid being removed with the pipette, the tap is again opened, and mercury permitted to flow in until the globe is quite filled. The rest of the process is continued as usual. Where several densities are to be determined in succession, this process saves more time than would readily be believed.

Fig. 2.



The compression tap used in this experiment is capable of withstanding a very considerable pressure of mercury, and is so manageable that the smallest portion of metal may be added at will; it is also particularly well adapted for various volumetric and gaseous operations. The following is the method of construction. A block of wood (fig. 2), *a*, *b*, *c*, *d*, has a square hole mortised in it, through which passes the vulcanized tube, *e*, *f*, *g*, *k*, attached at *e*, *f* to the lower orifice of the burette. A piece of hard wood, *i*, *k*, also passes through the mortise, and is retained in its place by the flange *i*. It is evident that on turning the head of the screw, *l*, the piece *i* will be pressed against the vulcanized tube and collapse it.

In order to facilitate comparison of the indifferent hydrocarbons from Boghead naphtha with the radicals, I annex the following Table, containing their boiling-points and densities in the fluid and gaseous state, according to various observers.

Comparative Table of the Physical Properties of the Radicals.

Radicals.	Boiling-Points.					Densities.				Vapour-densities.				
	Frankland.	Kolbe.	Wurtz.	Brazier and Gossleth.	C. G. Williams.	Frankland, at 11°.	Kolbe, at 18°.	Wurtz, at 0°.	C. G. Williams, at 18°.	Frankland.	Kolbe.	Wurtz.	C. G. Williams.	Theory.
					Mean.									
Propyle	...	...	...	...	68°	...	...	...	0·6745	...	...	...	2·96	2·97
Bntyle...	...	108°	106°	...	119°	...	0·6940	0·7057	0·6945	...	4·053	4·07	3·88	3·94
Amyle...	155°	...	158°	...	159°	0·7704	...	0·7413	0·7365	4·899	...	4·956	4·93	4·91
Caproyle	...	...	202°	202°	202°	...	...	0·7574	0·7568	...	...	5·983	5·83	5·87

Philosophical Transactions, 1857.

Researches upon Aldehyde. By A. Lieben.

A current of dry muriatic acid gas is passed into pure aldehyde placed in a freezing mixture; absorption and increase of volume take place, and the liquid divides into two perfectly colourless strata. When the action is completed, the two strata are immediately separated, as they react upon each other.

The lower stratum is equal to about one-third of the one above it; it consists of water saturated with muriatic acid, and always retains a small quantity of the lighter liquid, which gives it a turbid appearance, and causes it to become brown when it is kept for some time. The aldehyde and muriatic acid gas employed being anhydrous, the water can only be due to a decomposition of the aldehyde.

The upper stratum forms a perfectly colourless and limpid liquid. When distilled several times over chloride of calcium, a pure product is obtained boiling between 241° and 243° F., of which the composition is—

	Found.		Calculated.
C	33·41	33·46	33·57
H	5·81	5·77	5·59
Cl	5·81	49·12	49·65

These numbers lead to the formula $C^8 H^8 Cl^2 O^2$. The theoretical density of vapour for a condensation of 4 vols. is =4·94, that found by experiment at 343° F. is =5·08.

This body possesses an odour resembling at once that of aldehyde and that of muriatic acid; it does not react immediately upon litmus paper, but the spot made upon blue paper reddens rapidly on exposure to the air. Density at 54°·7 F. = 1·1376.

The author proposes to name this body *oxychloride of æthylydene*, adopting for the group $C^4 H^4$ contained in aldehyde or in some of its derivatives, the name of *æthylydene*, to indicate its isomerism with æthylene.

The reaction producing this body is expressed by the following equation:—

$$2C^4H^4O^2+2HCl=\left\{\begin{matrix}C^4H^4,Cl\\C^4H^4,Cl\end{matrix}\right\}O^2+2HO.$$

Oxychloride of æthylydene does not mix with water, but forms an oil which remains at the bottom. When gently heated a decomposition takes place; the oil disappears completely without coloration, and muriatic acid and *aldehyde* are formed.

When treated with perchloride of phosphorus to replace the oxygen contained in the body by chlorine, no action takes place in the cold; but when the two subtances are heated for several hours in a sealed tube in the water-bath, a complete solution is effected. The author has not yet been able to separate the product of this reaction from the oxychloride of phosphorus formed at the same time. He remarks in conclusion, that his oxychloride of æthylydene is isomeric with the chlorætheral obtained by d'Arcet in the action of chlorine upon crude olefiant gas.—*Comptes Rendus*, March 29, 1858, p. 662.

On a New Product of the Decomposition of Iodoform with Potash. *By* A. Brüning.

If iodoform be dissolved in a little alcohol, brought into contact with a suitable quantity of solution of potash in a retort so that no separation of potash takes place, the potash allowed to react for a long time at a boiling temperature, the apparatus being so arranged that the vapours may always flow back, and the half be then distilled over, a distillate of a pleasant aromatic odour is obtained. Water separates oil-drops, which unite and form a reddish oily stratum. This is heavier than water, and when properly purified and dried has the

Composition, C^2HI^3O.—Its vapour-density was found to be 9·55 (calculated for 4 volumes of vapour 9·55), and the body consequently belongs to the few which with 4 vols. of vapour only contain 1 equiv. of oxygen. It boils at 358°—360° F., and solidifies in a crystalline form at 21° F. Spec. grav.=3·345, consequently the highest of all known organic compounds. Like mercury, this fluid does not moisten glass. When freshly prepared the body is colourless, but when exposed to the light, it soon becomes reddish by the separation of some iodine. It is readily soluble in alcohol and in æther, but not soluble in water, to which, however, it communicates a pleasant odour. As already stated with reference to its preparation, it is readily volatilized with aqueous and alcoholic vapours, although its boiling-point is much higher. When digested for a long time at a boiling heat in a sealed tube with ammonia or potash, the compound is readily decomposed into iodide of ammonium or potassium, and a formiate. It is also readily decomposed by metallic mercury in the presence of air and light. Nitrate of silver precipitates yellow iodide of silver immediately

from the alcoholic solution when heated, and when the boiling is continued there is an intermixture of metallic silver. Analysis gave,—

Carbon	4·39	4·59
Iodine	93·55	92·84

This body may be regarded as iodoform in which 1 equiv. of iodine is displaced by oxygen, thus—

Iodoform $(C^2 H) I^3$, the new body $(C^2 H) I^2 O$,

or as an oxide of the radical $\left.\begin{matrix} C^2 H \\ I \end{matrix}\right\}$.—Liebig's *Annalen*, civ. p. 189.

ANALYTICAL CHEMISTRY.

On a New Test for Potash. By W. Plunkett, *Student in the Evening Class for Practical Chemistry, Museum of Irish Industry**.

The two reagents, tartaric acid and bichloride of platinum, used by chemists for the detection of potash in its salts, do not either of them fulfil all the conditions required of a good test. Tartaric acid is neither sufficiently delicate nor sufficiently speedy in its action to render it a satisfactory test, whilst bichloride of platinum requires to be evaporated to dryness along with the solution under examination to render it sufficiently delicate in all cases; this requirement, together with its costliness, prevents it being employed by students in analytical classes.

In Mr. Galloway's 'Manual of Qualitative Analysis,' the fact is noticed that bitartrate of potash is soluble in acids; Fresenius also, in his 'Qualitative Analysis,' notices the fact, and adds that in the case of acid solutions the free acid must, if practicable, be expelled by evaporation and ignition, or the solution must be neutralized with soda or carbonate of soda, before we can proceed to test for potash with tartaric acid. It is evident, that whether we have a free acid or not, an acid must be set free whenever we add tartaric acid to a salt of potash, thus:—

$$KO, SO^3 + 2HO, \overline{T} = KO, HO, \overline{T} + HO, SO^3.$$

I was led by these two facts—1st, that a free acid is set free whenever tartaric acid is added to a salt of potash, and 2ndly, that bitartrate of potash is soluble in free acids—to try bitartrate of soda in place of tartaric acid. I anticipated that bitartrate of soda would prove a much more delicate and speedy test, because I considered that the liberation of a free acid was the cause of the want of delicacy and the slowness of action of tartaric acid, and in these anticipations I have not been disappointed, as the following experiments show.

Four solutions of sulphate of potash containing the following quantities were prepared:—the first contained 10 parts, the second

* Communicated by the Author.

5 parts, the third 2·5 parts, and the fourth 1·25 part of the salt in 1000 parts of water. The bitartrate of soda solution employed was prepared by dissolving a quantity of tartaric acid in water, dividing the solution into two equal parts, neutralizing one exactly with carbonate of soda, and then mixing the two solutions together. The quantity of potash solution employed in each experiment was 20 fluid grains.

With the first sulphate of potash solution, tartaric acid gave a precipitate immediately, after much agitation; bitartrate of soda gave with the same solution a copious precipitate after a very slight agitation.

With the second solution, tartaric acid gave a slight precipitate after much agitation, and after standing twenty-four hours; bitartrate of soda gave with the same solution a plentiful precipitate immediately after it had been well agitated.

With the third solution, tartaric acid gave no precipitate even after standing twenty-four hours; bitartrate of soda gave a distinct precipitate after much agitation almost immediately.

With the fourth solution, tartaric acid gave no precipitate even after long standing; bitartrate of soda gave a slight turbidity after much agitation and standing a short time; the quantity did not increase by long standing.

In order still further to prove the greater delicacy of the bitartrate of soda, I added tartaric acid to a solution of a salt of potash, and after agitating it very well I allowed it to stand for twenty-four hours; I then filtered off from the bitartrate of potash which had been formed, and added to the filtrate a solution of bitartrate of soda and agitated, when an immediate precipitate of bitartrate of potash was produced.

The acids may differ as to their capability of dissolving bitartrate of potash, it is therefore possible that if I had employed nitrate of potash or chloride of potassium instead of sulphate of potash in the experiments, the difference between the two tests, tartaric acid and bitartrate of potash, might not have been quite so marked as in the experiments I have given.

I need scarcely remark that bitartrate of soda cannot replace tartaric acid as a test when the solution to be tested contains a free alkali, because bitartrate of potash is soluble in free alkalies; but if the other bases are sought for, the solution cannot be alkaline when we arrive at the examination for potash, and it is not often that we have to deal with an alkaline solution, even when potash is the only base that is looked for.

This investigation was carried out in the laboratory of this Institution under the direction of Mr. Galloway.

On the Detection of very small Quantities of soluble Metallic Iodides.

By C. W. Hempel.

I. The fluid is put into a finely drawn-out tube of white glass, some perchloride of iron is added, and as much sulphuric acid as

will render the liquid colourless. It is then mixed with a very small quantity (about 2 drops to 5 cub. cent.) of a thin starch paste, prepared with boiling water and shaken round before being added, the tube is closed and the starch allowed to settle. The iodine is detected by the more or less reddish coloration of the starch (when seen upon a white ground).

Experiments.

Iodine (employed as KI).					coloured the starch
1. 0·00001	grm.	in 4	cub. cent.	water	brownish lilac.
2. 0·000003	„	5	„	„	orange.
3. 0·000002	„	5	„	„	faint orange.
4. 0·000001	„	2	„	„	strong rose-red.
5. 0·0000006	„	0·5	„	„	distinctly rose-red.
6. 0·0000001	„	0·5	„	„	pale rose-red.

In the first experiments the lowest stratum of starch was scarcely coloured, whilst the uppermost exhibited the strong coloration.

II. The fluid is placed in a vessel with a ground stopper, perchloride of iron and sulphuric acid is added, and then so much chloroform that the fluid when violently shaken is rendered very turbid after the disappearance of the air-bubbles. The chloroform is allowed to settle, the glass stopper is replaced by a cork hollowed out in the form of a funnel, into which a colourless tube drawn out into a fine point is inserted, and the vessel is turned upside down, when the chloroform collects in the tube and betrays the presence of iodine by its colour. With small quantities of iodine the colour is not always rose-red; as long as the chloroform has not flowed together, it is rather lilac. This colour is recognizable with larger quantities of iodine even in twilight, when the chloroform is held up to the light.

Experiments.

1. 0·0001 grm. of iodine in 200 cub. cent. of water gave a very strong violet-red colour to the chloroform.

2. 0·00001 grm. of iodine in 20 cub. cent. of water gave a very strong rose-red colour to the chloroform.

3. 0·000002 grm. of iodine in 3 cub. cent. of water gave a very strong lilac-rose colour to the chloroform.

4. 0·000001 grm. of iodine in 3 cub. cent. of water gave a very strong lilac-violet colour to the chloroform.

5. 0·00002 grm. of iodine in 400 cub. cent. of water mixed with 6 drops of a moderately concentrated solution of perchloride of iron and a few drops of sulphuric acid gave a distinct rose colour to the chloroform.

0·000001 grm. of iodine is capable of giving a distinct rose colour to the chloroform, as may be easily proved in the following way. The iodide of potassium is put into a tube (not drawn out) of about 0·5 cub. cent. capacity; water and acidulated perchloride of

iron are added until the tube is half-filled; it is then agitated with a drop of chloroform, and the tube is completely filled with water. If the tube be corked and held horizontally over a white porcelain surface, the drop of chloroform appears distinctly rose-red.

To prove that even when greatly diluted perchloride of iron decomposes hydriodic acid, the author took 0·000004 grm. of iodine and 5 cub. cent. of water, added to it 0·05 cub. cent. of a very dilute, acidulated solution of perchloride of iron, and agitated the whole with 2 drops of chloroform. The latter acquired a strong rose colour. The same experiment repeated with starch, again exhibited the appearance above described; the upper stratum alone was coloured (orange).—Liebig's *Annalen*, February 1858, p. 260.

On the Deportment of Phosphate of Sesquioxide of Chromium with Ammonia and other Reagents. By JOHN DOWLING *and* W. PLUNKETT, *Students in the Evening Class for Practical Chemistry, Museum of Irish Industry**.

Gmelin in his 'Handbook of Chemistry,' has not described any of the properties of the phosphate of sesquioxide of chromium, we were therefore induced to study the behaviour of this salt with some of the more common reagents. We prepared it by adding to a solution of sesquichloride of chromium a solution of ordinary phosphate of soda. Phosphate of the sesquioxide of chromium is precipitated as a bluish-green amorphous substance, which becomes green when dry. It is easily soluble in the mineral acids, but insoluble in acetic acid; its insolubility in this latter acid distinguishes it from the sesquioxide of chromium, which it resembles so much in its colour and other properties; phosphate of chromium and its oxide resemble therefore the phosphates of iron and alumina and their oxides in their behaviour with acetic acid. It is precipitated unchanged from its acid solutions by sulphide of ammonium, and also by ammonia; a small quantity of it frequently dissolves in the ammonia, just as the sesquioxide of chromium does, communicating, like the oxide, a puce tint to the fluid. It dissolves, like the sesquioxide, in cold solutions of the fixed alkalies, and is precipitated, like the oxide, on boiling the liquid.

Phosphoric acid, when in combination with sesquioxide of chromium, may be as readily overlooked in analytical inquiries as when the acid is associated with alumina or iron; the acid can be readily and safely detected, if a portion of the precipitate produced by the general reagent of the chromium group be fused with nitrate of potash and carbonate of soda, and the fused mass dissolved in water acidulated with nitric acid, and subsequently a mixed solution of chloride of ammonium, ammonia, and sulphate of magnesia be added to it: there will, of course, be no need to look for phosphoric acid, if the fused mass shows no signs of chromium when tested in the ordinary way.

* Communicated by the Authors.

THE CHEMICAL GAZETTE.

No. CCCLXXVI.—June 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Oxides of Cerium. *By* R. BUNSEN.

THERE still exists a doubt whether the body obtained by the calcination of protoxalate, protonitrate, or protocarbonate of cerium, and also by that of the hydrated protoxide in contact with the air, is peroxide or protoperoxide of cerium.

The following experiments show that when protoxalate of cerium, prepared from perfectly pure compounds of cerium, is ignited in contact with the air in a platinum crucible, there remains a protoperoxide, which is white, with a scarcely perceptible tinge of pure citron-yellow, only observable by daylight. When heated, this oxide acquires a deep orange-red colour, but regains its original colour on cooling. Boiling concentrated sulphuric acid dissolves the body to form an orange-red salt, which, on cooling, becomes pale yellow, and dissolves in water with a yellow colour. Muriatic and nitric acids have but little action upon it even when boiling. When calcined in hydrogen, the yellowish-white colour becomes permanently converted into olive-green, without any perceptible decrease of weight. This protoperoxide possesses the remarkable property of dissolving even in the cold, and still more readily when warmed, in a mixture of iodide of potassium and muriatic acid, with evolution of heat and separation of iodine. This property may be employed to ascertain its composition. But as doubts still exist as to the exact atomic weight of cerium, Jegel has determined it by the aid of this reaction. For this purpose the neutral protosulphate was employed; it may be prepared pure and analysed by the following methods. Chemically pure basic persulphate of cerium is digested with dilute sulphuric acid and sulphurous acid until it is completely dissolved; the fluid is evaporated to dryness, the saline residue heated until all excess of sulphuric acid is driven off, and the salt is twice recrystallized from water.

1·5726 grm. of the air-dried salt thus prepared, dissolved in water, acidulated with muriatic acid, and precipitated by oxalic

acid, gave, after standing for two days in a warm place, a precipitate of protoxalate of cerium, which, when calcined in an open crucible, left 0·7899 grm. of pure, sandy, yellowish-white protoperoxide of cerium. No trace of protoxide could be detected by ammonia in the fluid, even after long standing. Chloride of barium added to the strongly acidified solution, produced a precipitate of 1·6185 of sulphate of baryta, which was only filtered after standing for 24 hours, and contained no trace of oxalate of baryta. 0·2760 grm. of the protoperoxide obtained were sealed hermetically into a glass flask with muriatic acid free from chlorine, and pure iodide of potassium; the flask contained so little air that its oxygen could not amount to 0·0003 grm. After everything was dissolved, the separable oxygen, s, corresponding with the oxide present, was determined iodometrically in accordance with the method of Bunsen (Liebig's *Annalen*, lxxxvi. p. 265), by means of the equation

$$s=\frac{O}{J}a(nt-t').$$

The experiment gave $n=2$; $t=24·2$; $t'=9·5$; $a=0·0055886$, which gives the following composition for the protoperoxide of cerium:—

I. Protoxide of cerium	95·04
Oxygen	4·96

Starting from this composition of the calcined oxide, the analysis of the sulphate gives—

II. Protoxide of cerium	57·49
Sulphuric acid	42·51

The atomic weight of cerium calculated from this analysis, by means of the capacity for saturation of sulphuric acid, is therefore 576·3 (O=100). Starting from this atomic weight, we then also get as the atomic composition of the protoperoxide I.—

	Found.		Calculated.
Cerium	80·99	3	81·21
Oxygen	19·01	4	18·79

The experiment repeated with 1·6967 grm. of the sulphate gave—

0·8504 grm. protoperoxide of cerium,
1·7500 grm. sulphate of baryta.

0·3429 grm. of this protoperoxide gave $n=4$; $t=14·2$; $t'=11·0$; $a=0·005588$, whence follows:—

Protoxide of cerium	95·07
Oxygen	4·93
Protoxide of cerium	57·46
Sulphuric acid.....	42·54

Atomic weight of cerium..... 575·25.

Composition of protoperoxide of cerium:—

	Found.		Calculated.
Cerium	80·99	3	81·21
Oxygen	19·01	4	18·79

Next to the protosulphate, the protoxalate is best fitted for the determination of the equivalent of cerium. An experiment was therefore made with this by Jegel. The salt employed was precipitated by pure oxalic acid from a solution of protoxide of cerium, boiled for a long time with sulphurous acid, after the addition of muriatic acid. As the salt obtained does not give off all its water even at 320° F., at which point it begins to be decomposed, it was analysed like the sulphate, with an undetermined amount of water after drying at 212° F. The analysis gave—

Protoxide of cerium	94·87
Oxygen	5·13
Oxalic acid	39·98
Protoxide of cerium	60·02

Atomic weight of cerium..... 575·65.

Composition of protoperoxide of cerium:—

	Found.		Calculated.
Cerium	80·83	3	81·21
Oxygen	19·17	4	18·79

All these experiments show that the compound produced by the ignition of the oxalate in the air, has a composition agreeing, *within the limits of error in the experiments*, with the formula $CeO + Ce^2 O^3$. The precautions to be observed in the preparation of the oxide, in order that it may approach most closely in composition to this formula, will be easily ascertained by further experiments with larger quantities of substance.

The deviations from this formula are, however, sufficiently small, to allow of the behaviour of protoperoxide of cerium towards muriatic acid containing iodide of potassium being employed for its iodometric determination where it occurs *in large quantities*. For this purpose the substance to be examined is weighed in a long-necked glass flask of 10—15 cub. cent. capacity, a few fragments of pure iodide of potassium are added, the neck of the flask is drawn out to a narrower orifice by the blowpipe-lamp, the flask is filled up to the narrow part of the neck with muriatic acid free from chlorine and perchloride of iron, and a small fragment of carbonate of soda is added in order to displace the last portion of air by carbonic acid; the flask is then hermetically sealed, and heated on the water-bath until the compound of cerium is entirely dissolved. The amount of iodine separated is then determined by an iodometric analysis. Retaining the denominations for the elements of the analysis described by Bunsen, the amount of protoxide of cerium present, x, is obtained from the formula

$$x = \frac{3(Ce+O)}{J} a(nt - t').$$

The volumetric determination of peroxide of cerium in its compounds will be described hereafter, when the oxide itself is taken into consideration.

The average of the values (576·3, 575·3, and 575·7) found by

experiment, gives for the equivalent of cerium 575·8. This number must be very near the true atomic weight of cerium. Further experiments are in progress to establish it with more accuracy.

The above-described analysis of the peroxalate of cerium obtained by precipitation from an acid solution, differs considerably from that found by Dr. Kjerulf* for the salt obtained by dissolving hydrated protoxide of cerium in oxalic acid. The agreement of the atomic weight calculated from the preceding analyses with that deduced from the sulphate, shows, however, that the salt analysed by Kjerulf contained an intermixed basic salt. As the calculation of the equivalent of cerium from Kjerulf's analysis rests on the assumption that the salt was neutral, the value found could not be correct.—Liebig's *Annalen*, January 1858, p. 45.

On the Action of Nitric Acid upon Phenic Acid.
By J. Fritzsche.

If 2 parts of crystallized phenic acid be dissolved in 100 parts of hot water, mixed with 3 parts of fuming nitric acid of spec. grav. 1·570 (50° B.) and distilled, the fluid becomes brown, and there is formation of ammonia, hydrocyanic acid, and

Nitrophenic Acid, $C^{12} H^5 NO^6$.— This is obtained when the distillate is saturated with ammonia and distilled. A golden-yellow fluid passes over, containing the volatile ammoniacal salt of this acid, together with phenate of ammonia. If it be then again distilled with a little sulphuric acid, the mixture of these two acids passes.

If the brown fluid, produced by the addition of the acid to the solution of phenic acid, be heated to boiling, the action is very violent, a resin is formed, which causes concussive ebullition, and nitrophenic acid passes in drops with the aqueous vapours, when distillation is effected. The author performed this distillation in a platinum apparatus specially adapted to this purpose.

When the above-described proportions are employed, a large quantity of nitrophenic acid passes first of all in drops, and afterwards dissolved in water.

If a smaller quantity of nitric acid be made use of in proportion to the phenic acid, little or no solid nitrophenic acid is obtained, but principally a yellow oleaginous product, which remains fluid even at 32° F. This is still to be investigated.

A larger proportion of nitric acid, up to a certain point, has no injurious influence upon the formation of the volatile nitrophenic acid, only in this case the residue contains, with the humoid acids, a smaller proportion of the new acid, but principally binitrophenic acid. Trinitrophenic acid requires for its formation a far larger excess of nitric acid, and it has never yet been possible to separate it from the products of the action of dilute nitric acid upon phenic acid; at the utmost its presence might be concluded from the bitter taste.

The aqueous fluid passing simultaneously with the nitrophenic acid in the above process, contains hydrocyanic acid as a subsidiary

* Liebig's Annalen, lxxxvi. p. 265, and lxxxvii. p. 17.

product. If the distillation be very long continued, especially with a somewhat larger proportion of nitric acid, a crystalline product makes its appearance at last in the distillate; this, however, is not nitrophenic acid, but binitrophenic acid, which is volatilized in small quantities with the aqueous vapours from concentrated solutions; small quantities of this acid are also usually obtained as a residue, when the fluid from which the nitrophenic acid has been separated by filtration and subsequent distillation, is evaporated at a gentle heat.

The residue in the distilling vessel, consisting of two parts, a reddish-yellow fluid and the above-mentioned resinous mass, contains a new acid and ammonia.

Nitrophenic acid is the same body described by A. W. Hofmann as nitrophenole, and obtained by him in the action of nitrous acid upon aniline and of nitric acid upon phenole; it is also the same body mentioned by the author as early as 1839, when he obtained it in small quantity by treating indigo with nitric acid.

Nitrophenic acid is a crystalline body of a pale yellow colour, with a slightly greenish tinge, an aromatic odour resembling that of burnt sugar, and a sweet aromatic taste. At 113° F. it forms a yellow, transparent oil, and solidifies again at this temperature to form a crystalline mass. This melting-point is rather higher than that given by Hofmann (107°·6 F.), and the point of solidification even differs by 34°·2 F., for which the author can only account by the assumption that Hofmann, in his experiments on fusion, employed a preparation which was not quite pure, but contained an intermixture of the above-mentioned oleaginous acid. The author's experiments were made with perfectly pure acid crystallized from æther, with a quantity of 15 grms. and with a thermometer made by Greiner, jun. of Berlin; they gave concordant results, whether the acid was fused by itself or under water. The boiling-point of the acid was found with the same thermometer to be 417°·2 F., consequently nearly the same as that found by Hofmann (420°·8 F.).

Nitrophenic acid is but very sparingly soluble in water at ordinary temperatures; but when shaken with water, even perfectly free from ammonia, it furnishes a distinctly yellow solution, which possesses a sweetish aromatic taste, and distinctly reddens blue litmus-paper. At an elevated temperature its solubility is considerably increased; even from a solution saturated at the melting-point of the acid, fine, acicular crystals separate during cooling to 32° F., and a solution saturated at a still higher temperature becomes turbid when cooled at first by separation of small drops of fluid acid, but afterwards long acicular crystals are formed in it.

In alcohol, nitrophenic acid is readily soluble even at ordinary temperatures, but far more so at an elevated temperature; and a solution saturated at a boiling heat solidifies entirely on cooling into a mass consisting of acicular crystals, containing the mother-liquor absorbed as in a sponge. From more dilute solutions the acid shoots into long shining needles, but the author could not obtain measurable crystals from alcoholic solutions.

In æther, nitrophenic acid is much more soluble than in alcohol

at ordinary temperatures, and at a high temperature this solubility is considerably increased. Benzine and sulphuret of carbon behave similarly. Analysis gave—

C	51·87	12	=900·00	51·80
H	3·66	5	62·50	3·60
N	..	1	175·06	10·07
O	..	6	600·00	34·53

By combination with bases, nitrophenic acid forms compounds the colour of which is either splendid scarlet or orange; many salts possess both colours, but then the variously coloured salts are distinguished by their amount of water. The affinity of nitrophenic acid for bases is less than that of carbonic acid, as it is only capable of expelling carbonic acid in particular cases; and on the other hand, small quantities of carbonates separate by exposure to the air from perfectly neutral solutions of the salts of calcium, strontium, and barium. Hofmann states that when potash, soda, or ammonia is poured over nitrophenole, it is immediately converted into crystalline compounds of a splendid scarlet colour; the author can only confirm this as to colour, with regard to soda; the potassium-salt separated by an excess of the base was always obtained of an orange colour, and the ammonium-salt could only be obtained of an orange colour similar to that of the potassium-salt. In a preliminary notice the author mentioned that the potassium-salt obtained in a thin layer by evaporation upon a glass plate exhibits a dichroism, appearing of an orange colour only by transmitted light, but by direct light bluish-green (it must rather be called golden-green); he now adds that this dichroism is peculiar to certain surfaces, and that the sodium-salt exhibits the same phænomenon, but in a less degree. The author prepared the

Potassium-salt, $C^{12} H^4 KNO^6 + HO$, containing 22·07 of potassium and 4·68 of water, in flat, orange-red needles; also the

Ammonium-salt, in orange-yellow crystals; the *sodium-salt*, in scarlet needles; the *barium-salt*, $C^{12} H^4 Ba NO^6$, with 33·09 of barium; the *strontium-salt*, $C^{12} H^4 Sr NO^6 + 3HO$, with 23·70 of strontium and 13·16 of water. The *calcium-salt*, $C^{12} H^4 Ca NO^6 + 4HO$, with 12·64 of calcium and 19·00 of water. Also the *magnesium-* and *zinc-salts*, the *copper-salt* (orange-yellow), the *lead-salt* and *silver-salt*.

The *silver-salt*, $C^{12} H^4 Ag NO^6$, was obtained in two forms, in prismatic crystals and needles; the needles are first produced and afterwards become converted into prisms.

Solutions of nitrophenates give a deep orange-red precipitate with a solution of nitrate of silver; with concentrated solutions this appears to a certain extent gelatinous, at least to the naked eye, as it is described by Hofmann, but when examined by the microscope it always shows a crystalline stucture, and usually consists first of all of needles.

The silver-salt is obtained with certainty by the following process:—1 part of nitrophenic acid is dissolved in a slight excess of

caustic ammonia, and the solution is mixed with water until it amounts to 100 parts; 2 parts of crystallized nitrate of silver is also dissolved in 100 parts of water, and the two solutions are mixed together. When too little ammonia has not been used, neither turbidity nor precipitate is produced at the first moment, but in a short time long needles of a deep red colour are formed and almost entirely fill the fluid; then orange-coloured prisms gradually make their appearance among these needles, the precipitate sinks to the bottom, and after some time it is entirely converted into a thin stratum of granular crystals lying on the bottom; these may be easily washed, and constitute a perfectly pure preparation. It is of the more importance to obtain such a compound directly, as the salt is partially decomposed during recrystallization; for when boiled with water, the fluid becomes blackened, free acid making its appearance, and a black silver precipitate being deposited, by which a considerable loss is caused. This decomposition also continues partially in the solution filtered whilst boiling hot, which passes through the filter clear and of an orange-red colour, but becomes distinctly darker whilst cooling, for which reason also the crystals obtained by recrystallization are rarely pure red, but usually somewhat blackish. Such dingy crystals were obtained by the author even from the solutions above described, when they were heated before the concentration only to 122° F. Analysis gave 28·91 of carbon, 1·66 of hydrogen, and 43·48 of silver.

The *æthyle-salt* was obtained by the author by decomposing the silver-salt with iodide of æthyle, extracting the mixture with æther, and evaporating the extract, by which means a brown, oleaginous fluid was procured. This was distilled, when the æther passed undecomposed as a wine-yellow fluid, and only left a small carbonaceous residue. It is almost inodorous, nearly insoluble in water, but readily soluble in alcohol and in æther. When boiled with solution of potash it is only decomposed with difficulty.—*Bull. de St. Pétersb., Classe phys.-math.* xvi. p. 161.

On the Preparation of Tetræthylurea. By A. Brüning.

The author brought sulphate of tetræthylammonium in contact with cyanate of potash, evaporated the solution, and extracted the residue with alcohol. The alcoholic solution had an alkaline reaction; it was evaporated and furnished crystals. These effervesce with acids from the evolution of carbonic acid. When dissolved in muriatic acid and mixed with perchloride of platinum, they furnished the platino-chloride of tetræthylammonium with 29·6 of platinum (calculated 29·4). From this it follows that the cyanic acid was decomposed into carbonic acid and ammonia, and that in this way no urea with 4 equivs. of alcoholic radical was obtained. The author made this experiment, because Hofmann obtained a crystallized body by the treatment of oxide of tetræthylammonium with cyanic acid, which he supposed to be tetræthylurea.—Liebig's *Annalen*, civ. p. 200.

On the Fermentation of Tartaric Acid. By L. PASTEUR.

PART I.—The author shows, that as there is an alcoholic ferment which exists wherever sugar is split into alcohol and carbonic acid, and a lactic ferment which is always present when sugar is converted into lactic acid, the fermentation of tartaric acid leads to a similar result.

It has long been known that crude tartrate of lime left to itself in water is capable of fermentation. Noellner investigated the products of this fermentation, and ascertained the existence of an acid which he considered to be new; of this Nicklès gave the exact composition, and MM. Dumas, Malaguti and Leblanc, in their work upon the hydrocyanic æthers, found it to be identical with the metacetonic acid obtained by Gottlieb by the action of potash upon sugar.

The author's experiments have been made upon tartrate of ammonia instead of tartrate of lime, and this change of base has induced changes in the composition of the products, with other curious peculiarities. In the present memoir he does not advert to these, but confines himself to the study of the cause of the phænomenon.

He operates as follows:—Pure tartrate of ammonia is dissolved in distilled water, to which some soluble nitrogenous matter is added, to the extent of 2—3 thousandths of the total weight of the solution. The perfectly limpid liquid is placed whilst very hot in a bottle which is filled up to the neck, and when its temperature has fallen to about 86° F., a few cubic centimetres of the turbid liquid of a good fermenting tartrate is added. The quantity of solid matter thus added is perfectly imponderable, but it nevertheless has a great influence. If the proper conditions of temperature and the neutrality or slight alkalinity of the liquid be well maintained, the whole liquid will be turbid in a few hours, and the fermentation will be indicated on the following day by an evolution of gas.

The turbidity of the liquid and the evolution of gas increase by degrees, and a deposit is gradually formed at the bottom of the vessel. This deposit is excessively small in proportion to the tartrate. The evolution of gas diminishes after attaining its maximum. By the optical examination of the liquid, it is very easy to follow the gradual conversion of the tartaric acid into products which have no action upon polarized light. The deposit is found under the microscope to consist of small needles or granules of small diameter, united in masses, in irregular flakes, held together by a glutinous matter. The diameter of the granules or globules is the same as in lactic yeast, and the general appearance of the two products under the microscope is very analogous. The deposit washed with much water and placed in a solution of tartrate of ammonia in pure water, causes its fermentation.

PART II.—Racemic acid is formed by the combination of one molecule of dextro- (or ordinary) tartaric acid, with one molecule of lævo-tartaric acid. The chemical properties of these two tartaric acids are so identical that they cannot be distinguished, except in the presence of matters which act upon polarized light.

It was therefore interesting to see whether racemic acid would undergo the same fermentation as ordinary (right) tartaric acid, and whether the ferments above described would effect the transformation of lævo-tartaric acid as readily as that of the ordinary acid. Racemate of ammonia was treated as above; the fermentation was set up with the same facility, the same characters, and the deposition of the same yeast. But when the progress of the phænomenon is studied with the aid of polarized light, it is found that things go on very differently. After a few days of fermentation, the liquid, which was at first inactive, possesses a sensible rotatory power to the left, which increases by degrees as the fermentation continues. When this has attained its maximum there is no trace of dextro-acid in the liquid, which when evaporated and mixed with its volume of alcohol, immediately furnishes an abundant crystallization of lævo-tartrate of ammonia.

We see here the character of molecular dissymmetry proper to organic matters intervene as modifying the affinity in a physiological phænomenon. There is no doubt that it is the kind of dissymmetry peculiar to the molecular arrangement of the lævo-tartaric acid that is the sole cause of the non-fermentation of this acid in conditions in which the inverse acid is destroyed.

The intimate cause of the difference here indicated appears probably to be due to the rotatory power of the matters which enter into the composition of the ferment. If the ferment consists of dissymmetric matters, it will not accommodate itself equally to an aliment which is itself dissymmetric in the same or an opposite direction; just as the dextro-tartrate of quinine differs essentially from the lævo-tartrate of that base, which is active, whilst the dextro- and lævo-tartrates of potash, or any other inactive base, are chemically identical.—*Comptes Rendus*, March 29, 1858, p. 615.

Facts relative to the various States of Sulphur separated from its Combinations. *By* S. Cloëz.

It is generally admitted that certain bodies may exist in their various combinations in two opposite states, playing in some the part of an electro-negative or acid element or body, and in others that of a combustible, electro-positive or alkaline element. It may be asked, whether the essentially relative electrical states of the combined bodies manifest themselves by sensible differences in the properties of the isolated bodies. As regards sulphur, in particular, is there a constant relation between the part played by this body in its combinations and the different states which it presents after its separation? This question has lately been answered in the affirmative by M. Berthelot.

The author has recently made some observations which prevent him from sharing in this opinion. The following is a summary of his experiments.

I. *Sulphur extracted from the Chlorides or Bromides of Sulphur.*—Fordos and Gélis were the first to observe the formation of

insoluble amorphous sulphur by the decomposition of the chloride in the presence of water. With an excess of water, renewed several times in the course of five or six days, the sulphur separated is almost perfectly insoluble in sulphuret of carbon; it only contains 0·12—0·20 of soluble, crystallizable sulphur. Very different results are obtained when the decomposition of the chloride is effected very slowly; the sulphur obtained may then contain as much as 0·95 of soluble and crystallizable sulphur. This is done by exposing the chloride to the air in a corked tube with the point drawn out and broken, or in an imperfectly corked bottle. The reaction is not completed for a very long, but of course variable time, according to the humidity of the air, which alone causes the decomposition of the chloride. The sulphur crystallizes as it separates, and it is obtained at last in the form of large octahedral transparent crystals, sometimes covered with a thin coat of amorphous, opake, insoluble sulphur.

Bromide of sulphur behaves in the same way, but its decomposition is slower.

Thus the chlorides and bromide of sulphur produce insoluble sulphur by a rapid, and soluble sulphur by a slow decomposition.

II. *Sulphur of the Hyposulphites.*—The chemical constitution of hyposulphurous acid may be regarded in two different ways,—either the sulphur occurs in it, as in sulphurous and sulphuric acids, entirely in the state of a combustible body; or if we consider this acid as a compound of sulphurous acid and sulphur, analogous to sulphuric acid formed of sulphurous acid and oxygen, the sulphur performs a double part in it,—it exists partly as an electro-positive, and partly as an electro-negative body. Whichever hypothesis be adopted, it must be capable of verification, if it be true that there exists a constant relation between the electro-chemical function of the combined sulphur, and the different conditions of solubility of the free sulphur. The experiments made with the view of solving this question have led to no decisive result; the only conclusion to be drawn from them is, that the insoluble sulphur is generally obtained by a rapid separation, whilst the soluble sulphur is usually formed in slow decompositions.

The yellow product of the action of an excess of muriatic acid upon crystallized hyposulphite of soda, is soluble in dilute muriatic acid. The filtered solution is clear, scarcely presenting a slight opaline tint. Nearly all the alkaline salts render this solution turbid and precipitate its sulphur; the sulphates of potash and ammonia especially possess this property in the highest degree.

The same substance retains water and sulphurous acid. After exposure for eight days *in vacuo* over sulphuric acid, it is still elastic and furnishes a considerable quantity of water by the action of heat; it cannot therefore be regarded as pure sulphur.

Hyposulphite of soda, dissolved in water, is decomposable by the action of the pile; there is a formation of sulphur which adheres to the positive pole, as in the electrolysis of sulphuretted hydrogen The decomposition takes place in the same way after the addition of

sufficient soda to render the solution strongly alkaline. This circumstance, combined with the adherence of the sulphur to the platinum electrode, shows that the current first decomposes the salt into base and acid, and acts secondarily upon the latter, producing sulphurous acid which passes to the negative pole in the form of sulphite.

III. *Sulphur of Hydrosulphuric Acid and the Sulphurets.*—Most oxidizing bodies decompose hydrosulphuric acid and the sulphurets, separating the sulphur in a soluble or insoluble state according to the mode of operation. The same compounds are decomposable by the pile; the sulphur separated is completely soluble according to Berthelot. The polysulphurets decomposed by acids also furnish soluble, crystallizable sulphur.

Sulphuric acid, the alkaline sulphurets, the fixed caustic alkalies and their carbonates and ammonia, possess the property of modifying insoluble amorphous sulphur, and bringing it to the condition of soluble and crystalizable sulphur; this is a very common disturbing cause, of which it is necessary to be aware. This is evidently the cause of the solubility of the sulphur extracted from sulphuretted hydrogen by means of the pile; in this case no relation can be established between the state of the sulphur separated and the part assigned to it in the compound. This also applies to the sulphur extracted from the polysulphurets by the action of acids.

Without these conditions, hydrosulphuric acid, the sulphurets, and the compounds in which sulphur is considered to act as an electro-negative element, may furnish insoluble, electro-positive or combustible sulphur. The insolubility of this sulphur cannot be attributed to the oxidizing bodies which serve to isolate it. The author thinks it more rational to assume that the soft, insoluble state is the normal state of sulphur, representing, as it were, the nascent state, only this condition is not very stable; it is modified in a great many physical and chemical circumstances, especially when the decomposition takes place slowly, or when the product separated comes in contact at the moment of its formation with reagents capable of changing its condition.

IV. *Sulphur extracted from Oxysulphoarsenic Acid.*—This acid, obtained by M. Bouguet and the author in combination with potash, must be considered as arsenic acid in which 2 equivs. of oxygen are replaced by an equivalent proportion of sulphur. It is analogous in its constitution to the chlorosulphuret of phosphorus of Sérullas, or the oxychloride discovered by Wurtz.

The composition of the potash salt is represented by the formula

$$AsO^3\,S^2,\ KO\,2HO.$$

When this salt is treated with an excess of concentrated muriatic acid, it is immediately decomposed, furnishing soft sulphur. The sulphur isolated is almost perfectly insoluble in sulphuret of carbon; it contains less than 0·06 of crystallizable, soluble sulphur; the reaction takes place, however, without elevation of temperature, and without the oxidizing conditions which furnish insoluble sulphur with hydrosulphuric acid and the sulphurets.

The aqueous solution of the salt is easily decomposed by the action of the pile; the sulphur deposited at the positive pole differs essentially from the product obtained at the same pole by the electrolysis of hydrosulphuric acid; it is soft, elastic, and perfectly insoluble in sulphuret of carbon.

The insolubility of the sulphur separated from the oxysulpharseniate of potash confirms the author's view of the state of this simple body at the moment of its separation; it also shows that this state is independent of the electro-chemical function which it is considered to fulfil in its compounds.—*Comptes Rendus*, March 8, 1858, p. 485.

On the Action of Bromine upon Fulminating Mercury.
By M. Kekulé.

The author first refers to his previous experiments upon fulminating mercury, from which he concluded that it is a nitrated cyanogen compound, and that its relations to chloroform and chloropicrine would be most simply expressed by the formula

$$C^2(NO^4)(C^2N)Hg^2.$$

He mentions the opinion expressed at the same time by Schischkoff with regard to the constitution of this body, according to which the formula should be doubled, and fulminic must be regarded as nitroacetonitrile + 2 cyanic acid:—

$$C^4H^2(NO^4)N + 2C^2NO^2H.$$

He cites a number of the arguments adduced by Schischkoff in favour of the doubled formula, and shows that such arguments are not sufficient for the establishment of the molecular formula, and that, if carried out to its consequences, it would lead to an endless and useless duplication of a great number of chemical formulæ.

As the distinction between Schischkoff's formula and that proposed by the author, consists, on the one hand, in its supposing the molecular formula to be twice as great, and on the other, in its assuming $\frac{1}{4}$th of the nitrogen in fulminating mercury to be contained therein as a nitro-group, whilst Kekulé supposes half the nitrogen as forming such a nitro-group, it became important to seek for reasons in favour of one or the other opinion by analysis. Determinations of the nitrogen by the method of Will and Varrentrapp, in which the nitrogen of the nitro-group is not, or is very imperfectly obtained in the form of ammonia, gave results which lay exactly in the middle between the numbers required by the formulæ of Schischkoff and the author. As, however, the nitrogen was found in smaller amount than is required by Schischkoff's formula, and as the method cannot, in any case, give too little nitrogen, but must rather always furnish too much, the experiments are evidently opposed to Schischkoff's formula.

The author finds an essential support for his opinion in the behaviour of fulminating mercury towards bromine. Thus, if bromine be allowed to act upon fulminating mercury under water, perbro-

mide of mercury is formed, and without any evolution of carbonic acid a body is produced, which may be regarded as fulminating mercury in which the mercury is replaced by bromine. This beautifully crystallizable substance, *dibromnitroacetonitrile*, which from its analysis and chemical behaviour possesses the composition—

$$C^2 (NO^4) (C^2 N) Br^2,$$

stands therefore, from its mode of production, in very near relation to fulminating mercury; in its properties also it exhibits the greatest analogy with chloropicrine and bromopicrine, and stands to a certain extent in the middle between fulminating mercury and bromopicrine:—

Fulminating mercury.... $C^2 (NO^4) (C^2 N) Hg^2$.
Dibromnitroacetonitrile.. $C^2 (NO^4) (C^2 N) Br^2$.
Bromopicrine..... $C^2 (NO^4) Br . Br^2$.

It consequently approaches closely to the previously described series of compounds, to which also the two bodies, very recently discovered by Schischkoff, nitroform and trinitroacetonitrile, may be added:—

Nitroform..... $C^2 H . (NO^4) (NO^4) (NO^4)$.
Trinitroacetonitrile $C^2 (NO^4) (C^2 N) (NO^4) (NO^4)$.

The author also indicates that fulminating mercury and the newly discovered dibromnitroacetonitrile may be compared on the one hand with acetonitrile $= C^4 H^3 N$, but that just as acetonitrile is regarded as cyanide of methyle $= C^2 H^3 . C^2 N$, these two bodies may be considered to be nitroproducts of the methyle series containing cyanogen, and consequently compared with bromopicrine, chloropicrine, and chloroform.

In conclusion, the author also states that an aqueous solution of isocyanurate of potash treated with bromine furnishes carbonic acid in abundance, a circumstance which speaks strongly against Schischkoff's view that fulminic acid contains more cyanic acid than isocyanuric acid:—

Fulminic acid.	Isocyanuric acid.
$C^4 H^2 (NO^4) N$	$C^4 H^2 (NO^4) N$
$C^2 N \quad O^2 H$	$C^2 N \quad O^2 H$
$C^2 N \quad O^2 H$	

because, according to this view, twice as much carbonic acid should evidently be obtained from fulminating mercury than from isocyanurate of potash, whilst it actually only furnishes traces of carbonic acid.—*Verhandl. des naturhist.-medicinischen Vereins zu Heidelberg, vom* December 21, 1857.

On Siliciuret of Manganese. By Professor Wöhler.

Professor Brunner has lately made the interesting observation that the manganese reduced by sodium from the fluoride, possesses perfectly different properties from that reduced from the oxide by charcoal. It has greater hardness, takes as fine a polish as steel, and retains its lustre unchanged in the air, whilst the metal reduced in

the ordinary way is soon reduced to pulverulent oxide when exposed to the air, and decomposes water even at ordinary temperatures. Another very remarkable circumstance is the low melting-point of the metal reduced by sodium, which does not appear to be higher than that of ordinary cast iron.

The author received from Brunner a very beautiful regulus of this manganese, and with it a few fragments, with which he undertook some experiments. On solution in muriatic acid, this metal left a filmy, white, light substance, which the author, who was at the moment occupied with investigations upon oxide of silicium, readily recognized as that oxide. It possessed all its characteristic properties; it was dissolved with a violent evolution of hydrogen gas by caustic potash and hydrofluoric acid, and when heated in the air it smouldered away to silicic acid. (In the preparation of silicium already described by Wöhler, it was always observed that when silicium freed from all aluminium by muriatic acid was treated with hydrofluoric acid, a strong evolution of hydrogen gas immediately occurred. This is due to oxide of silicium, formed by the portion of silicium which had been chemically combined with the aluminium.) Hence it was probable that the different properties of the manganese thus prepared were caused by the presence of silicium, produced by the action of the fluoride employed upon the substance of the crucible.

These observations were completely confirmed by Brunner*. His discovery appeared to the author only to acquire increased interest in this way; he therefore immediately undertook various experiments with the view of obtaining a manganese richer in silicium, and if possible a compound constituted in accordance with definite equivalent proportions. These experiments were carried on in a blast-furnace with a good draught, at about the temperature of the melting of pig-iron: Hessian crucibles were employed.

A mixture of about equal parts of fluoride of manganese, soluble glass, cryolite, and sodium, was pressed firmly into a dry crucible and covered with a mixture of chlorides of potassium and sodium. After the reduction had taken place with a considerable noise, the fire was increased. A single, well-fused regulus was obtained; it was very hard and brittle, with indications of a laminar-crystalline structure on the fracture, but without the separation of visible, free silicium, such as is always observed when aluminium is employed.

This manganese is far less violently attacked by muriatic acid than that received from Brunner, each fragment soon becoming coated with a grayish crust of oxide of silicium, which had to be frequently rubbed off, or removed by solution of potash, in order to complete the solution. The oxide of silicium thus formed is far more dense than that produced from a manganese containing less silicium, or from protochloride of silicium. It is not crystalline, however, as was shown by microscopic examination.

As it was probable that the hydrogen gas evolved from this metal, although it did not ignite spontaneously in the air, might contain

* See Chem. Gaz., No. 373, p. 178.

siliciuretted hydrogen, the gas, after being dried by a chloride of calcium tube, was passed through a narrow glass tube heated to redness in one place. Within 10 minutes a fine brown speculum of amorphous silicium was formed, a proof that during the solution of siliciuret of manganese in muriatic acid, as in the case of aluminium containing silicium, a small quantity of siliciuretted hydrogen gas is formed.

As might have been expected, this siliciuret of manganese was completely dissolved by hydrofluoric acid, with a violent evolution of a hydrogen gas of disagreeable odour.

According to the analysis effected by Küpke with 1·076 grm. in which the silicium was obtained and weighed as silicic acid, this metal contained 11·7 per cent. of silicium.

Another experiment was made with a mixture of fused protochloride of sodium and manganese, fluor spar, soluble glass and sodium. A well-fused, very brittle regulus was again obtained; it enclosed a few small vesicular spaces, lined with steel blue prismatic crystals. This siliciuret of manganese, analysed by Küpke, gave 13 per cent. of silicium, which nearly corresponds with the equivalent proportion $Mn^5 Si$, according to which it should contain 13·37 per cent. of silicium.

In two experiments made on a tolerably large scale with protochloride of sodium and manganese, silicofluoride of potassium and sodium without fluoride of calcium, and with a stronger and better maintained fire, no trace of metal was obtained, although from the noise produced at first it might have been supposed that a reduction was taking place. It would almost appear, therefore, as if in this case the manganese had again reduced the sodium from the chloride of sodium formed, whilst it was not capable of decomposing the fluoride of sodium.

Another experiment was made with a mixture of fused protochloride of manganese, fluoride of calcium, silicofluoride of potassium and sodium, covered with chlorides of potassium and sodium. The regulus obtained was almost silvery white and extremely brittle, and possessed a conchoidal, strongly shining fracture. The first two properties are perhaps due to the circumstance that it was not allowed to cool slowly. This metal only contained 6·48 per cent. of silicium.

In a last experiment, a mixture of protochloride of manganese, sodium, fine quartz sand and cryolite was employed, the two latter in the proportion of 22 : 26 (in equivs.=4 : 1). The regulus exhibited indications of a laminar structure, and had a yellowish white tinge. However, it only contained 11·37 per cent. of silicium.

In the manganese prepared according to his method without the addition of any siliceous compound, Brunner found the amount of silicium in twelve different specimens to vary between 0·6 and 6·4 per cent. He also attempted to increase the amount of silicium by the employment of silicofluoride of potassium or even of silicic acid, and in this way obtained a metal with nearly 10 per cent. of silicium. On the other hand, however, he endeavoured particularly to solve the question whether the presence of silicium was the cause of the different properties of the metal prepared by his method, or whether

it was only an accidental constituent and without any influence upon these properties. The decision of this question was very difficult, as the experiments had to be carried on in ordinary earthen crucibles. Nevertheless he succeeded in reducing the amount of silicium to about $\frac{1}{10}$th per cent, by fusing the coarsely powdered manganese for about 10 minutes with chloride of sodium to which 1 per cent. of chlorate of potash had been added. He remarks upon this, —"With this we must be contented for the present, until we have crucibles which cannot give off any silicium. Moreover, I have not observed that the properties of the manganese were essentially altered by this intermixture (at least within the limits observed). The colour, fusibility, hardness, and lustre remained pretty much the same in the different samples."

Hence, either the metal reduced by charcoal from the oxide is impure, and indebted for its difficult fusibility and ready oxidizability to a foreign admixture as Brunner supposes, or this is really the pure metal, and so extraordinarily small an amount of silicium is sufficient to change the properties of the metal so essentially. This would be sufficiently wonderful; but the author is nevertheless inclined to admit it, especially as we already know something very similar with regard to iron, in its various states of wrought iron, steel, and cast iron.—*Nachrichten von der G. A. Univ. und der K. Gesellsch. der Wiss. zu Göttingen*, 1858, p. 59.

On the Action of the Alkalies upon Sulphocyanide of Æthyle. *By* A. Brüning.

The author enclosed sulphocyanide of æthyle with aqueous solution of potash or baryta in glass tubes, and heated them to 212° F. The oily body on the surface of the aqueous stratum did not disappear, and from the analysis it appeared that bisulphuret of æthyle had been formed. The aqueous stratum contained cyanide of potassium and cyanate of potash.—Liebig's *Annalen*, civ. p. 198.

ANALYTICAL CHEMISTRY.

Investigation of the oxidizing properties of the Permanganate of Potash, and on the Determination of several Mineral Acids. *By* L. Péan de Saint-Gilles.

The author has found, that to render the reactions of permanganate of potash complete, two conditions are often necessary:—

1st. The permanganate must be added in excess;

2nd. The liquids operated on must be alkaline or acid according to circumstances.

In this way the complete and almost instantaneous conversion may be effected in the cold, of hyposulphites, sulphites, and sulphurets into sulphates, of free iodine and iodides into iodates, of nitrites into nitrates, and of arsenites into arseniates. The determination of these compounds is rendered very easy by the introduction of some simple

modifications into the process of Margueritte; these consist in the employment of the two following reagents:—

1. A normal solution containing about 25 grms. of crystallized permanganate of potash to 2 litres of water. This liquid will keep for several months, without alteration, when protected from the light of the sun.

2. A solution consisting of about 1 litre of water, 100 grms. of crystals of sulphate of iron, and 100 cub. cent. of sulphuric acid free from nitrous compounds. This excess of acid slackens the oxidation of the protosalt of iron by contact with air. The volume of the solution of permanganate decolorized by a constant volume of the sulphate of iron is determined from time to time.

The liquid to be tested is mixed, according to circumstances, with an alkaline carbonate or an acid; an excess of permanganate is poured in, sufficient to give an intense red colour to the liquid which covers the precipitate of oxide of manganese which is usually formed. If the liquid be alkaline it is then rendered alkaline, and a known volume of sulphate of iron is added to dissolve the peroxide; then the permanganate is added again, until the appearance of the rose tint. The result is calculated by reading off upon the lunette, the total volume of permanganate employed, and simply deducting the quantity decolorized by the sulphate of iron.

Sulphurous and Hyposulphurous Acids.—Sulphites and hyposulphites react imperfectly upon the permanganate in the presence of an excess of acid. In this case there is produced a mixture of sulphuric and hyposulphuric acids nearly in the proportion of 4 : 1. In oxidizing the hyposulphites, all deposition of sulphur may be avoided by pouring the neutral hyposulphite into the permanganate rendered acid. In alkaline liquids the phænomenon is different; the sulphites absorb exactly 1 equiv., and the hyposulphites 4 equivs. of oxygen, becoming entirely converted into sulphates. The determination is thus very accurately effected.

Hyposulphuric Acid.—The hyposulphates of baryta and soda met with in commerce usually contain traces of sulphites or hyposulphites which decolorize the permanganate. On adding to their solutions an excess of this reagent, the new crystals deposited by the liquids furnish pure hyposulphuric acid, which has no action upon the permanganate, even when supersaturated by an alkali.

Hydrosulphuric Acid.—In the presence of an alkaline carbonate, the soluble sulphurets and the greater part of the metallic sulphurets absorb 4 equivs. of oxygen and become converted into sulphates. A very small quantity of sulphur frequently escapes this reaction, an inconvenience which appears to be due to the precipitation of a little sulphuret of manganese retained by the precipitate of oxide. In this case the liquid decolorized by the sulphate of iron is slightly milky, and this is always an indication of incomplete oxidation.

Hypophosphorous Acid.—Hypophosphite of baryta approaches the hyposulphites by its action upon the permanganate. When decomposed by sulphuric acid, the acid set free absorbs an amount of oxygen insufficient for its conversion into phosphoric acid. The author's results nearly correspond with the proportion $P^3 O^{14}$, inter-

mediate between phosphatic acid, $P^3 O^{13}$, and phosphoric acid, $P^3 O^{15}$. Phosphoric acid itself reacts upon the permanganate.

Iodine and Hydriodic Acids.—The permanganate furnishes to iodine 5 equivs., and to the iodides 6 equivs. of oxygen to form iodic acid, $IO^5 HO$, which has no action upon the acid protosulphate of iron. The operation ought to be effected in an acid liquid, but the oxidation is more rapid in the presence of alkalies, and in this case no notice need be taken of the presence of chlorides or bromides which do not react. The determination is very exact, and may be applied to the examination of commercial iodides of potassium, which often contain 2 or 3 per cent. of iodate of potash.

Hydrocyanic Acid.—Free hydrocyanic acid does not decolorize the permanganate, but when supersaturated with an alkali it absorbs a proportion of oxygen which varies with the alkalinity of the liquid; the amount appears to be always between 2 equivs. corresponding with cyanic acid, and 4 equivs.

Sulphhydrocyanic Acid.—Sulphocyanide of potassium, $KCyS^2$, is oxidized in a more definite manner than the cyanides. This salt absorbs 8 equivs. of oxygen in alkaline, and only 6 equivs. in acid liquids; this difference might have been foreseen, as the cyanides do not react in the presence of acids.

$$KCyS^2 + 2(KO) + O^8 = KO, CyO + 2(KOSO^3),$$
$$HCyS^2 + 2(HO) + O^6 = HCy + 2(SO^3HO).$$

Nitrous Acid.—The determination of nitrous acid is founded on the following facts:—

1. Very dilute sulphuric or nitric acid may be poured into a solution of a nitrite, without giving rise to an appreciable loss of deutoxide of nitrogen. This would not be the case if the nitrite were poured into the acid.

2. An excess of permanganate completely transforms nitrous acid into nitric acid. If the permanganate were dropped into the nitrous acid, the limit of the reaction would not be clearly perceived, as the decoloration is much reduced towards this limit. The determination of nitrites is effected with great accuracy in acid liquids.

Arsenious Acid.—The preceding observations apply perfectly to arsenious acid, which may be determined with equal accuracy in alkaline and acid liquids. The reddish colour due to the formation of a manganic salt, when the permanganate is poured into the arsenious acid, renders the use of the sulphate of iron indispensable.

Determination of the Strength of the Permanganate.—The strength of the solution of permanganate may be determined very accurately by means of metallic iron, but this operation is tedious and delicate. Arsenious acid, hyposulphite of soda, and iodine may serve for this purpose, but the author prefers oxalate of ammonia, a well crystallized salt, not hygroscopic and easily purified. Hempel has shown that oxalic acid decolorizes permanganate of potash as distinctly as the protosalts of iron, and this reaction, which only requires the application of a gentle heat and the use of a certain excess of sulphuric acid, is capable of the greatest accuracy.

The strength is usually estimated by the volume of liquid decolo-

rized by 1 grm. of iron. This form complicates the calculations when the chameleon is employed otherwise than for iron. It would be better to take as the base the oxygen furnished by the permanganate to reducing bodies. Thus 350 would be the value of a liquid containing 1 grm. of oxygen in a volume of 350 cub. cent. This number, divided by 7, gives exactly the value of the same liquid in relation to 1 grm. of iron.—*Comptes Rendus*, March 29, 1858, p. 624.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Note on a new Process of Painting with Oxychloride of Zinc. By M. Sorel.

In 1855 the author brought before the Academy of Sciences various products obtained by means of oxychloride of zinc, including cements as hard as marble and quite insoluble in water, and a paint, also insoluble, which he expected to take the place of painting in oil and other materials. This mode of painting was difficult of application, requiring, like silicious paintings, the employment of a liquid to fix the last layer; on increasing the drying properties of the paint to avoid the use of this liquid, the paint thickened very rapidly in the vessel, so that there was no time to apply it. The author has now succeeded in getting over these difficulties.

The liquid which forms the vehicle in this mode of painting, is an aqueous solution of chloride of zinc, in which an alkaline tartrate is dissolved. To give tenacity to the picture, gelatine or starch is added to the liquid, and converted into paste by heating the latter; the heat must not be sufficient to convert the starch into dextrine or glucose.

The pigments employed must consist in great part of oxide of zinc, the ordinary colours being added in the necessary proportions.

The advantages of the process are stated by the author as follows:—1. It does not require to be ground, the powder is merely suspended in the liquid; 2. it is more beautiful than painting in oil and equally solid; 3. it has no odour and dries very rapidly, so that a layer may be applied every two hours in winter and every hour in summer; 4. it resists damp and even boiling water, and may be soaped like oil-paint; 5. it is antiseptic on account of the chloride of zinc which it contains, and adapted to preserve wood from rot; 6. it possesses in a high degree the property of diminishing the combustibility of wood, paper, &c.; and 7. there is no danger in its employment or application.

The author also exhibited a new translucent plastic matter composed of potato-starch and hydrated chloride of zinc, the latter being of such a density as to swell the starch without dissolving it. To modify its hardness and render it more or less white or opake,

certain salts or powders, such as oxide of zinc, sulphate of baryta, &c. are added. This plastic matter is prepared in the cold by mixing the starch and other substances with the chloride of zinc. The substance moulds perfectly and solidifies in the mould like plaster. The objects thus formed are diaphanous like horn, bone, or ivory; to obtain it diaphanous very little of the pulverulent matters are to be added, except sulphate of baryta, as this salt, although insoluble, gives very little opacity to the material. This is not the case with oxide of zinc and carbonate of lime. To protect the objects from moisture, they are covered with one or two coats of good varnish. It may receive any colour, and may be obtained of any degree of hardness, even supple, like India-rubber, but not elastic.—*Comptes Rendus*, March 1, 1858, p. 454.

Dried Yeast and its Adulteration.

Dried yeast, which has been repeatedly patented, is usually prepared on a large scale, and diffused by commerce. Such manufactories are in operation especially in England, France, Sweden, Bavaria, Flanders, &c. The yeast is washed with water, pressed in sacks to remove all water, and spead out upon linen, in order to dry it in the air, in the sun, or in heated chambers, or upon plates of slightly burnt gypsum, which imbibes the water. It is turned from time to time, and the larger fragments are broken up. Yeast cakes also occur in commerce now; they were first prepared in North America, but have already been repeatedly imitated. This yeast is prepared in the following way:—about 3 ounces of hops are mixed with nearly 4 quarts of hot water and 3½ lbs. of rye-meal; as soon as this hot infusion has cooled to a luke-warm temperature, ½ a pint of yeast is added to it, and the whole is left to ferment. The next day 7 lbs. of maize- or barley-meal (or pease-meal) are added, and the whole is kneaded into a stiff dough, which is rolled out into large cakes of half an inch thick, and cut up (usually with a glass knife) into smaller cakes. These are dried in heated chambers or in the sun, with frequent turning; they are then sent into the market in air-tight packages. To use this yeast, a little of it is broken off, softened in hot water, and left standing for 12 hours in a warm place; it is then employed like ordinary yeast. The yeast may even be preserved in a similar way by adding starch-meal, and working it into dry cakes, which are then perfectly desiccated. In dried yeast or yeast cakes, the starch-corpuscles of the intermixed meals are always recognizable under the microscope, together with the vesicles of fermentation.

An extensive fraud is generally practised with this dried yeast. It is often mixed with chalk and potato-starch, and sometimes consists principally of meal. As much as 35—40 per cent. of potato-starch has been found, and this in a yeast which was furnished to a pastry cook; in France a distiller found as much as 67 per cent., and Chevallier found the vessels in a yeast manufactory filled with potato-starch.—*Würzburger gemeinnützige Wochenschrift*, and *Polyt. Centralbl.* 1858, p. 224.

THE CHEMICAL GAZETTE.

No. CCCLXXVII.—July 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Piperic Acid. *By* Professor VON BABO *and* E. KELLER.

If piperine be treated on the water-bath with an alcoholic solution of caustic potash (1 part of piperine, 3 parts of hydrate of potash, 12—20 parts of absolute alcohol) in a flask united with a refrigeratory apparatus in such a manner that the products of distillation may flow back, the fluid acquires a brown colour, and in the course of a few hours fine, shining scales separate. On opening the apparatus the characteristic odour of piperidine is observed. If the above mentioned treatment be continued until the formation of the scales ceases, which is the case in about 12 hours with 30 grms. of piperine, the whole of the piperine is decomposed, as may be seen from the fact that a sample of the fluid is no longer precipitated by water. To separate the products formed, the crystalline laminæ are freed from the mother-liquor as far as possible by a strainer and the use of the centrifugal machine. By the distillation of the mother-liquor, the retort being closely united with a receiver and a Woulf's bottle containing muriatic acid, the alcoholic solution of a strong base is obtained; this, after saturation with muriatic acid and evaporation, crystallizes in beautiful, extremely fine needles, of nearly an inch in length, such as are described by Cahours and Anderson for the muriate of piperidine. This salt, mixed with perchloride of platinum, furnishes on evaporation or precipitation by alcohol a platinum double salt, the amount of platinum in which agrees exactly with that of the chloride of platinum and piperidine of Cahours, so that, as the other properties of the base agree with those of piperidine so far as these are described, the authors have no hesitation in regarding it as piperidine. The residue in the retort consists almost exclusively of caustic potash, coloured brown by a resinous mass, which, when sufficiently concentrated, separates partially as resin, and appears to be identical with the aldehyde resin produced by the action of caustic potash upon alcohol. At least, when the caustic potash is saturated by an acid, it exhibits,

on the application of heat, the characteristic odour of the product formed from aldehyde under similar circumstances.

The crystalline laminæ consist of the potash salt of a non-nitrogenous acid. By this treatment, therefore, piperine is simply decomposed into a base and an acid, which is called piperic acid by the authors. With regard to the composition of piperine and its products of decomposition, this investigation leads to the conclusion that the formula of piperine is most probably $=C^{70}H^{40}N^{2}O^{12}$. Thus it belongs to the type $2NH^{4}O$. The authors suppose that 2 atoms of hydrogen are displaced by two unknown radicals A and B, the sum of which $=C^{10}H^{10}$, so that the expression for piperine and its decomposition into piperic acid is twice the following:—

$$N\left\{\begin{matrix}\left.\begin{matrix}A\\B\end{matrix}\right\}=C^{10}H^{10}\\ \left.\begin{matrix}C^{25}H^{9}O^{5}\\H\end{matrix}\right\}=C^{25}H^{10}O^{5}\end{matrix}\right\}N+2HO=C^{10}H^{11}N+C^{25}H^{11}O^{8}.$$

Piperic Acid, $C^{50}H^{22}O^{16}$.—It is precipitated by sulphuric or muriatic acid, in a gelatinous form, from the purified potash-salt. The precipitate appears composed of fine needles under the microscope. It was of a sulphur-yellow colour, and could not be obtained colourless. The acid is purified by recrystallization from alcohol.

Obtained in this way it is almost insoluble in water, difficult of solution in cold alcohol (1 part of acid requires 275 parts of absolute alcohol), readily soluble in boiling alcohol, from which it crystallizes on cooling, and difficult of solution in cold and hot æther; it is nearly insoluble in sulphuret of carbon and in naphtha, but rather more soluble in benzole. Solid at ordinary temperatures, it fuses at about 300° F., and sublimes partially at about 392° F.; a brown, fused residue remains, whilst the sublimate possesses a distinct odour of cumarine. When heated in the open air it burns, diffusing an odour very similar to anise; the coal left burns with difficulty.

Although the solution of the acid scarcely reddens litmus, it combines with bases to form well-characterized salts, from which it may be separated unchanged by the addition of an acid.

When brought in contact with nitric acid, even if the latter be very weak, it is converted into an orange-coloured nitro-body which has not yet been carefully investigated, but which, when heated with potash, diffuses the same odour of cumarine observed by Anderson when piperine is treated in the same way, and ascribed by him to a volatile base. It is decomposed by concentrated sulphuric acid with the blood-red colour characteristic of piperine, after which carbonization takes place. With chlorine, bromine, and iodine products of substitution are formed; these require further investigation. When brought in contact with perchloride of phosphorus, the acid is immediately decomposed. A body of a vermilion-red colour is formed, and this also appears to be produced by the action of terchloride of phosphorus upon piperine. In a few days the mixture, which was at first solid, becomes fluid with formation of

oxychloride of phosphorus, whilst vermilion-red crystals separate from the fluid. From deficiency of material, this interesting reaction could not be pursued further. Analyses:—

	I.	II.	III.	IV.
C	=66·88	66·08	66·74	66·39
H	4·80	4·83	5·06	5·14
O	28·32	22·09	28·20	27·47

From these the following formulæ may be calculated:—

C^{50}	=300	66·37	C^{50}	=309	66·67	C^{26}	=156	67·24
H^{24}	24	5·31	H^{22}	22	4·89	H^{12}	12	5·17
O^{10}	128	28·32	O^{16}	128	28·44	O^{8}	64	27·59

Of these formulæ the authors think that the second, $C^{50}H^{22}O^{16}$, is to be preferred.

Piperate of Potash, $C^{50}H^{20}O^{14}$, 2KO, crystallizes in laminæ, which are remarkable for their peculiar lustre. They appear to belong to the rhombic system. The salt is readily soluble in boiling, but less so in cold water, is difficult of solution in alcohol, and almost insoluble in æther. When dried it loses no water of crystallization, and when heated to a higher temperature in the air, it smoulders away very quickly, leaving a coal which is difficult of combustion; during this process a distinct odour of anise is evolved. An attempt to isolate the substance by which the odour of anise is produced by the dry distillation of the potash-salt was unsuccessful. Analyses:—

	I.	II.
C	=55·76	56·70
H	3·94	3·32
O	24·43	21·49
KO	16·47	17·89

From these the following formulæ were calculated:—

C^{50}	=300	56·75	C^{50}	=300	56·97
H^{22}	22	4·16	H^{20}	20	3·80
O^{14}	112	21·19	O^{14}	112	21·26
2KO	94·6	17·90	2KO	94·6	17·97

Piperate of Soda, obtained by dissolving the acid in a hot solution of soda, from which it is precipitated as a white crystalline powder, is difficult of solution in cold, but readily soluble in hot water. The aqueous solution is precipitated by alcohol. The solubility of this salt is so small, that the acid might be employed as a reagent for soda. Pure piperate of potash produces a turbidity even with a concentrated solution of chloride of potassium, to which about 2 per cent. of chloride of sodium has been added.

Piperate of Ammonia.—If aqueous ammonia, as concentrated as possible and previously heated, be mixed with as much piperic acid as will dissolve in it, and then filtered and left to cool, piperate of ammonia crystallizes in colourless laminæ of a splendid satiny lustre, which possess the greatest similarity with cholestearine. Under the microscope rhombic tables may be detected; but the crystallization is too confused to be more exactly defined. When exposed in

a moist state to the air, the ammoniacal salt is decomposed, acquiring a pale yellow colour by separation of acid. But if it be dried under a bell-glass over lime to which a little muriate of ammonia has been added so as to form an atmosphere of ammonia, it loses no more ammonia even when placed over sulphuric acid *in vacuo*, but the decomposition above referred to reappears in moist air. If it be heated to 212° F. in a test-tube, a separation of ammonia commences, and increases considerably at a higher temperature, until at about 356°—392° F. the salt is decomposed with evolution of the above-mentioned anise-like odour, and formation of products which have not yet been minutely investigated, but amongst which there appears to be an alkaloid. No evolution of aqueous vapour was observed at the temperature of complete decomposition. If the salt be exposed for a long time to a temperature of about 302° F., and then dissolved in water with the addition of potash, it is completely dissolved; on the addition of muriatic acid, the acid separates again unchanged. Analysis:—

	Found.		Calculated.			
C	=61·77	C^{50}	=300	61·73	C^{50}	=300 61·97
H	5·05	H^{24}	24	4·94	H^{22}	22 4·54
O	26·22	O^{16}	128	26·34	O^{16}	120 26·45
NH^3	6·96	$2NH^3$	34	6·90	$2NH^3$	34 7·04

Piperate of Baryta.—This salt is produced by mixing a pure solution of piperate of potash with chloride of barium or some other soluble baryta-salt; it forms a white precipitate, consisting apparently of a light powder, whilst under the microscope it is found to be composed of very fine needles. It is slightly soluble in boiling water, and is thrown down again on the cooling of the solution; but this solubility cannot be made use of for its purification, it is too small (1 part requires at least 5000 parts of water for its solution), and moreover a partial decomposition of the salt appears to take place. The salt was therefore prepared for analysis by mixing a pure solution of piperate of potash with chloride of barium, and carefully washing the precipitate. The salt was dried *in vacuo* at 212° F. It gave on analysis:—

	Found.			Calculated.			
	I.	II.					
C	=51·05	51·05	C^{50}	=300	51·09	C^{50}	=300 51·26
H	3·78	3·78	H^{22}	22	3·75	H^{20}	20 3·41
O	19·88	18·85	O^{14}	112	19·07	O^{14}	112 19·14
BaO	25·29	26·32	2BaO	153·2	26·09	2BaO	153·2 26·19

Piperate of Lime.—If a solution of the potash-salt be mixed with chloride of calcium, the lime-salt is thrown down in the form of fine needles. It is somewhat more soluble then the baryta-salt in hot water. *Piperate of strontia* and *piperate of alumina* behave like the baryta-salt. On the addition of the potash-salt to salts of strontia and alumina, they are produced in the form of voluminous white precipitates.

Piperate of Magnesia.—When moderately dilute solutions of the potash-salt and chloride of magnesium are mixed together, no preci-

pitate is produced at first, and it is only after the lapse of some days that fine needles, 1 centimetre in length, of the magnesia-salt are deposited; in concentrated solutions these needles are immediately formed, but the authors did not obtain them in sufficient quantity for analysis.

Piperate of Zinc, obtained by mixing the potash-salt with chloride of zinc, forms a yellowish-white, caseous precipitate, which is insoluble in water.

Protopiperate of Manganese crystallizes in the form of small, silky laminæ of a yellowish colour.

Protopiperate of Iron is produced as a yellowish-white precipitate, which is soon oxidized, and acquires the colour of the persalts of iron.

Protopiperate of Cobalt is of a rose-red colour, without any definite crystalline form.

Piperate of Nickel forms a pale green, voluminous precipitate, insoluble in water.

Piperate of Cadmium forms a white pulverulent precipitate.

Piperate of Lead forms a yellowish precipitate, which, when heated, is slightly dissolved, and is thrown down again on cooling in the form of a crystalline powder.

Piperate of Copper is obtained when a solution of pure piperate of potash is mixed with sulphate of copper. The precipitate is extraordinarily increased by the addition of a few drops of ammonia; it consists of stellate groups of extremely fine, sky-blue needles. This salt is not simple in its constitution; it appears to be a basic salt, which agrees best with the formula $C^{100}H^{39}O^{23}+9CuO$. It may be a basic salt in which 9 atoms of water of 2 atoms of acid are replaced by 9 atoms of oxide of copper. But even with this assumption, the formula does not exactly agree with the found values. Analysis gave—

	Found.		Calculated.	
C	=49·67	C^{100}	=600	50·60
H	3·68	H^{39}	39	3·29
O	15·36	O^{23}	184	15·56
CuO	31·29	9CuO	360	30·55

Protopiperate of Mercury is produced as a white precipitate, which is reduced on the addition of ammonia, and

Perpiperate of Mercury, as a yellowish-white precipitate, which is converted into peroxide of mercury by the addition of potash.

Gold Compound?—On mixing a solution of chloride of gold (as neutral as possible) with piperate of potash, a yellowish-white precipitate is produced, from which metallic gold soon separates.

Piperate of Silver.—This salt is obtained by the precipitation of piperate of potash with nitrate of silver; it forms a colourless, scarcely crystalline powder, which, when dried, is but slowly blackened by the light. It is insoluble in the ordinary solvents. As the piperate of potash contained traces of muriatic acid, the solution of the salt was first mixed with a sufficient quantity of

nitrate of silver to precipitate all the chlorine as chloride of silver; this was then separated by filtration, and the filtrate treated with nitrate of silver. The precipitate was washed, dried at 212° F., and analysed.

C	=43·12	43·73	43·41	C^{50}	=300	45·04
H	2·87	2·97	3·21	H^{22}	22	3·31
O	18·23	17·94	18·02	O^{14}	112	16·81
AgO	35·78	35·36	35·36	2AgO	232	34·84

These numbers agree too little with the found values; but if we assume 1 atom more water in this salt, we have—

C^{50}	=300	43·80		C^{50}	=300	43·98
H^{24}	24	3·55		H^{22}	22	3·22
O^{16}	128	18·73		O^{16}	128	18·77
2AgO	232	33·92		2AgO	252	34·03

However, the salt still contains more silver than corresponds with the formula, which is probably due to its retaining a trace of nitrate of silver, which could not be entirely removed by washing.

Piperate of Piperidine is formed by dissolving the pure acid in a hot concentrated aqueous solution of piperidine; in concentrated solutions the salt separates as a thick crystalline paste, but when the solutions are more dilute, it forms colourless laminar crystals of a beautiful silky lustre. This salt also loses a small portion of its piperidine, just as the ammoniacal salt loses its ammonia, when left standing for a long time in the air, or over sulphuric acid, so that it then no longer dissolves entirely in water, and acquires a yellowish colour on the surface. When heated to 248° F., the salt fuses, without undergoing any change of composition; at a higher temperature piperidine is evolved, and the salt is entirely decomposed at about the same temperature as the ammoniacal salt. If the salt be exposed for a long time to a temperature of 302° F., it becomes partially insoluble in water; it still, however, dissolves instantaneously in caustic potash, and on the addition of an acid, the piperic acid is thrown down without alteration.

No amide could be prepared in this way. If the salt be treated with pentachloride of phosphorus, the result, as with pure piperine, or piperic acid, is a mass at first orange-yellow, afterwards becoming cinnabar-red with evolution of heat; this, when dissolved in water, deposits a body similar to the acid. The latter dissolves in potash with an odour of piperidine, and on the addition of muriatic acid, a yellowish body resembling piperic acid is thrown down. The authors hoped to have obtained in this way an amide of piperic acid, perhaps piperine, but did not succeed.

With the view of determining the quantity of piperidine, the salt was dissolved in absolute alcohol with the addition of a few drops of muriatic acid, as the platinum double salt may be regarded as insoluble in this fluid; the solution was mixed with perchloride of platinum, filtered, dried, and calcined. The elementary analysis was only performed eight days afterwards; during this interval the

salt had been standing over sulphuric acid, for which reason the amount of carbonic acid was found too small.

	Calculated.				Found.
C^{70}	=420	67·69	C^{70} =420	67·52	66·11
H^{44}	44	7·12	H^{46} 46	7·39	7·29
O^{16}	128	20·66	O^{16} 128	20·58	
N^2	28	4·53	N^2 28	4·51	
1 atom piperic acid		=452(C^{150})		72·67	
2 atoms piperidine		170		27·33	26·75
		622(C^{220})		100·00	

The results would agree more exactly with the calculation, if we were to assume an additional atom of water in the salt. The formula $C^{70}H^{46}O^{16}N^2 + HO$ requires 65·82 per cent. of carbon, 7·21 per cent. of hydrogen, and 26·64 per cent. of piperidine. But the salt loses no water in drying.

Piperate of Oxide of Æthyle is obtained when iodide of æthyle is allowed to act upon piperate of potash for a long time at a boiling heat; its formation takes place with difficulty, and is much assisted by the addition of absolute alcohol. To separate the æther, the alcoholic fluid, after the evaporation of the excess of iodide of æthyle, is mixed with a large quantity of water, and afterwards with a volume of æther equal to twice that of the alcoholic solution employed. Two strata are formed, the separation of which is facilitated by the addition of a few drops of caustic potash. The piperate of oxide of æthyle remains dissolved in æther; the ætherial solution is separated by means of the pipette from the aqueous fluid, and washed with water. The æther is allowed to evaporate, when the piperic æther remains in colourless crystalline scales. As far as the authors could observe with their small quantity of material, this does not appear to be volatile; at a high temperature it is decomposed, diffusing an abominable odour of acroleine. Its melting-point is about 168—172° F.—*Bericht über die Verhandl. der Gesellschaft zur Beförder. der Naturwissensch. zu Freiburg*, August 1856.

On the Bibasic Acids of the Series $C^nH^{n-2}O^8$. *By* C. Wirz.

For the preparation of the acids described in this memoir, the author employed the higher fatty acids of cocoa-nut oil, which remain in the retort after the distillation of the volatile acids in the decomposition of the soap prepared from that oil.

After the acids had been boiled for 14 days with nitric acid, the latter being constantly renewed when it became much weakened by boiling, the fatty acids acquired a different appearance. They no longer formed a cake at the surface, but a portion of them was deposited at the bottom as an oily stratum, which increased daily, until at last the entire mass solidified into a crystalline paste. This took place after the lapse of about 2 months, when the oxidation also appeared to be completed. The nitric acid is distilled off as completely as possible, the residue is treated with water, and the

fluid allowed to stand, when it forms, A, a yellow fluid which contains a number of acids in solution, and beneath this, B, an oily stratum, likewise consisting of products of oxidation and acids, formed by the nitric acid. These are separated from each other and from some fat which floats on the surface.

A. *The Yellow Aqueous Solution.*—It is evaporated in the water-bath until it solidifies into a crystalline paste. The author decomposes this mass first of all into 3 parts by fractional recrystallization. There separate—

a. A substance in white grains, which are soft to the touch;

b. As the second crystallization from the mother-liquors of the preceding substance, crusts consisting of grains or warts;

c. Finally, there remains a syrupous, yellowish-brown mass of peculiar odour, containing much nitric acid, which when evaporated becomes gelatinous, and does not crystallize any further.

The separate fractions are then further purified by recrystallization. As a solvent alcohol is finally employed; it is but slightly heated during the solution, in order to avoid the formation of æther. The author could then distinguish several substances by their physical properties, but soon found that the fractional crystallization of the acids was not sufficient for their separation; he attained his object, however, by preparing the silver-salts, and separating these by fractional crystallization. The silver-salts prepared from the substance *a*, by precipitating the acid saturated with ammonia by carbonate of silver, furnished the silver-salt of a new acid, which the author calls *lepargylic acid.* In the series of these acids it fills up the gap between sabacylic and suberic acids, and may be prepared in a pure state from the silver-salt.

Lepargylic Acid, $C^{18}H^{16}O^8$, forms small round granules. In appearance it resembles suberic acid, but its granules are harder. When fused upon platinum-foil it solidifies to form a minutely radiate, nacreous mass; whilst suberic acid on cooling after fusion, constitutes a more transparent crystalline mass, with longer rays. Its solubility in water is less than that of suberic acid. 100 parts of water at 64° F., dissolve 0·46 part of acid. Its melting-point, determined in a capillary tube, was found to be 239° F., but at this temperature only a portion was fused; the temperature rose to 255° F. before the whole contents of the tube were fused. Analysis:—

C	56·6	56·6	18	108	57·4
H	8·6	8·6	16	16	8·5
O	34·8	34·8	8	64	34·1

The Silver-salt, $C^{18}H^{14}Ag^2O^8$, is obtained in the form of a white powder by the precipitation of the solution of the ammonia-salt with nitrate of silver. It is readily altered when exposed to the air while moist. Dried at 212° F. it gave—

C	26·4	26·3	18	108	26·8
H	3·5	3·4	14	14	3·4
Ag	53·7	53·8	2	216	53·7
O	16·4	16·5	8	64	16·1

The Baryta-salt, $C^{18} H^{14} Ba^2 O^8$, obtained by saturating the acid with freshly precipitated carbonate of baryta, forms, after evaporation and desiccation over sulphuric acid, a white, porcelain-like mass. It is anhydrous. Analysis:—

C	..	..	..	18	= 108	33·7
H	..	..	..	14	14	4·3
Ba	42·3	42·2	42·2	2	137	42·4
O	..	..	..	8	64	19·6

The Æthylic Æther of Lepargylic Acid, $C^{26} H^{24} O^8$, was obtained by the passage of muriatic acid gas into an alcoholic solution of the acid. Analysis:—

C	63·7	26	= 156	68·9
H	9·9	24	24	9·8
O	26·4	8	64	26·3

From the mass *a*, which furnished the lepargylic acid, another portion was extracted by æther. 2 parts by weight of æther were poured over 1 part of it, and left standing for 24 hours, with frequent shaking, when the clear solution was poured away; the residue was again treated with æther, until, after this was repeated four times, the whole was dissolved. Each solution was evaporated by itself and kept separate, and a silver-salt was prepared from each; that of the first extract contained 52 per cent. of silver, that of the second 53·9 per cent., that of the third 55·5 per cent., and that of the fourth 57 per cent. The æther had consequently first dissolved principally the acids of the highest atomic weight; the acid separated from the first solution gave a silver-salt, which approached that of sebacylic acid. From the mother-liquor of lepargylic acid the author prepared,—

Suberic acid ..	$C^{16} H^{14} O^8$,
Pimelic acid ..	$C^{14} H^{12} O^8$,
Adipic acid....	$C^{12} H^{10} O^8$,
Lipic acid	$C^{10} H^8 O^8$,
Succinic acid ..	$C^8 H^6 O^8$.

Consequently the only acid wanting in this series, which commences with oxalic acid, $C^4 H^2 O^8$, is the member $C^6 H^4 O^8$ intervening between oxalic and succinic acids. The author points out with regard to this series, that each pair of members resemble each other in external appearance, the first and last members standing alone.

Oxalic acid
Succinic and Lipic acids
Adipic and Pimelic acids
Suberic and Lepargylic acids
Sebacylic acid.

The solubility of the acids diminishes with the elevation of the atomic weight, although from the experiments it does not appear that there is any constant decrease for the difference of $C^2 H^2$.

100 parts of water at 64° F. dissolve 0·46 parts of Lepargylic acid.
100 „ „ 64° F. „ 1·04 „ Suberic acid.
100 „ „ 64° F. „ 2·56 „ Pimelic acid.
100 „ „ 64° F. „ 7·73 „ Adipic acid.
100 „ „ 64° F. „ 10·56 „ Lipic acid.
100 „ „ 50° F. „ 20·00 „ Succinic acid
(Lecanu and Serbat).

The following differences were observed in the melting-points:—

Sebacylic acid	fuses at	260°·6 F.	
Lepargylic acid	„	234°·4 F.	10°·8 F.
Suberic acid	„	255°·2 F.	10°·8 F.
Pimelic acid	„	266°·0 F.	18°·0 F.
Adipic acid	„	284°·0 F.	19°·8 F.
Lipic acid	„	303°·8 F.	
Succinic acid	„	356°·0 F.	

With the exception of the last member, the melting-point of which is higher than that of the two preceding ones, the melting-point decreases with the elevation of the atomic weight, from 10°·8 to 19°·8 F.

With regard to lipic acid, the properties of which have not hitherto been distinctly characteristic, and the very existence of which has been doubted, and which was also regarded as identical with pyrotartaric acid, but afterwards distinguished therefrom, the author for the first time clearly defines its peculiarities, and also shows that it is not identical with pyrotartaric acid. It is a peculiar acid, and belongs to the place which was assigned to it by Laurent in the above series.

According to the author's investigations, lipic acid is essentially distinguished by its external appearance from the preceding members of the series, $C^n H^{n-2} O^8$. When crystallized from water, it forms translucent crusts, consisting of accumulations of round, hard warts, which are in their turn formed by the aggregation of small prisms. In a concentrated solution a portion of the surface of the fluid frequently crystallizes; the warts then produced are flat above, hemispherical beneath, and united in chaplets. When heated in a retort it furnishes an abundance of water, and then distils over, leaving a small carbonaceous residue. When the acid has once been distilled, it sublimes between two watch-glasses, even at a temperature of 212° F., forming long shining needles. When the distillation has been repeated sufficiently often, the acid is gradually converted into anhydride. The analyses of this acid lead to the formula $C^{10} H^8 O^8$, already proposed for it by Laurent.

Lipate of Silver, $C^{10} H^6 Ag^2 O^8$, forms a white powder. *Lipate of lime*, $C^{10} H^6 Ca^2 O^8$, when dried, forms a white opake mass. *Lipate of soda*, $C^{10} H^6 Na^2 O^8$, forms flat rhombic crystals. *Lipate of copper*, $C^{10} H^6 Cu^2 O^8$, was prepared by saturating the acid with carbonate of copper, as the solution of lipate of ammonia is not precipitated by sulphate of copper. A green solution was obtained, which deposited laminar crystals when evaporated; these were not

the neutral compound, but a mixture of the salt with uncombined acid. A weighed quantity of the green crystals was heated to between 302° and 392° F. in a platinum crucible until it no longer decreased in weight; by this means the uncombined lipic acid was expelled, and the residue was the neutral salt.

These are the acids obtained by the author from the crystallizations *a*, *b*, and *c* of the substance A.

The oleaginous substance B. appeared on examination to contain a mixture of nitrocapric acid, $C^{20} H^{19} NO^8$, and nitrocaprylic acid, $C^{16} H^{15} NO^8$. In the author's opinion, the formation of these nitro-acids effects the transition between the monobasic fatty acids and the bibasic ones produced from them by the action of nitric acid. The action of the nitric acid appears to take place by the production of lower acids from the higher fatty acids; these either become nitrated or distil over unchanged, as, for example, œnanthylic acid and its allies. A portion of the carbon probably escapes in the form of volatile products. In fact, at the commencement of the action of the nitric acid upon the fat, the red fumes are accompanied by the vapour of a peculiar body, which strongly affects the respiratory organs, as was observed by Bromeis in the treatment of margaric and oleic acids with nitric acid. By the further action of nitric acid upon these monobasic nitro-acids, the bibasic acids here treated of are formed.—Liebig's *Annalen*, civ. p. 257.

On some Salts of Cadmium. By Dr. Hugo Schiff.

The author describes the following new compounds of cadmium:—

Benzoate of Cadmium, $C^{14} H^5 CdO^4, 2HO$, obtained by dissolving carbonate of cadmium in benzoic acid. It dissolves in hot water, but is less soluble in alcohol.

Nitrobenzoate of Cadmium, $C^{14} H^4 (NO^4) CdO^4 + 2HO$, was prepared in the same way as the benzoate, and obtained on evaporation in laminæ of a micaceous lustre; these dissolved but sparingly in hot alcohol. It contains 13·5 per cent. of water, and 25 per cent. of cadmium. (Calculation gives 13·9 per cent. of water and 25·2 per cent. of cadmium.)

Cinnamate of Cadmium, $C^{18} H^7 CdO^4 + 2HO$, is thrown down on mixing the solution of a salt of cadmium with that of a cinnamate in crystalline flakes. It is insoluble in water, and sparingly soluble in hot alcohol. From the latter stellate groups of needles are obtained. It contains 8·1 per cent. of water and 25·1 per cent of cadmium. (Calculation gives 8·1 and 25·3 per cent.)

Succinate of Cadmium, $C^8 H^4 Cd^2 O^8$.—Carbonate of cadmium is added to a hot solution of succinic acid; it dissolves at first, and on a further quantity being added, a precipitate of the anhydrous salt in crystalline grains separates. It is insoluble in water and alcohol; and very sparingly soluble in succinic acid. It contains 48·6 per cent. of cadmium (calculated 49·1 per cent.).

Paratartrate of Cadmium (*Uvate*), $C^8 H^4 Cd^2 O^{12}$, is obtained in

the same way as the succinate, which it exactly resembles. It contains 42·7 per cent. of cadmium (calculated 43·0 per cent.).

Tannate of Cadmium.—A hot solution of tannic acid added to that of a salt of cadmium, gives a white precipitate, which becomes greenish-yellow during desiccation, and is insoluble in water and alcohol. The precipitate dried at 212° F. is anhydrous; it contains 21·4 per cent. of cadmium. Taking Strecker's formula of tannic acid, this would correspond with $C^{54} H^{19} Cd^3 O^{34}$; according to that proposed by Knop it would agree with $C^{36} H^{14} Cd^2 O^{22}$. The former requires 21·4, the latter 21·6 per cent. of cadmium.

Sulphate of Cadmium and Ammonia.—The crystallization obtained from the hot concentrated solution contained 24·05 per cent. of water (calculated 24·10 per cent.); the crystals obtained by gradual evaporation contained the same quantity.

Phosphamate of Cadmium, $NHPO^2, Cd, O^4 + 2HO$, is a white precipitate, which appears crystalline under the microscope. It contains 12·0 per cent. of water, 36·6 per cent. of cadmium, and 20·6 per cent. of phosphorus. (Calculated 11·9, 36·8, and 20·6 per cent.)

Sulphate of Cadmium and Magnesium, $S^2 CdMgO^8 + 6HO$.—When sulphuric acid is saturated, half with carbonate of magnesia and half with carbonate of cadmium, and the solution is evaporated, this double salt is obtained in oblique four-sided prisms. The salt is readily soluble in water. It contains 25·1 per cent. of water, 14·5 per cent. of sulphur, 26·1 of cadmium, and 5·5 of magnesium (calculation gives 24·8 HO, 14·7 S, 25·7 Cd, and 5·5 Mg).

Tartrate of Cadmium and Antimony.—A solution of potassio-tartrate of antimony gives a white precipitate with the solution of a salt of cadmium; this, when dried over chloride of calcium, lost 4·84 per cent. at 212° F. and 9·7 per cent. at 392° F. The salt dried at 392° F. gave 34·7 per cent. of antimony and 15·13 of cadmium. This corresponds with the formula $C^8 H^5 SbCdO^{16}$ for the air-dried salt, which requires 35·15 Sb and 15·26 Cd. The salt dried at 212° F. is $C^8 H^4 CdSbO^{14}$. (Loss of water found 4·84, calculated 4·9 per cent.) The salt dried at 392° F. is $C^8 H^2 CdSbO^{12}$. (Loss of water found 9·7, calculated 9·8 per cent.) The author regards the salt dried at 212° F. as $C^8 H^4 (SbO) CdO^{12}$, that is, as tartaric acid, in which one of the basic equivalents of hydrogen is replaced by the compound inorganic radical antimonyle, SbO. This salt is consequently an antimonylo-tartrate of cadmium.

The author considers that the salt dried at 392° F. is not to be compared with the anhydride of tartaric acid, as Gerhardt has done; he rather considers it probable that the antimonyle exists in it reduced to antimony. Its oxygen, combined with 2H, escapes as water, and then remains $C^8 H^2 SbCdO^{12}$.—Liebig's *Annalen*, civ. p. 325.

On the Amount of Caffeine in Coffee-beans.
By Professor A. Vogel, Jun.

The method hitherto employed for the extraction of caffeine from coffee-beans or tea-leaves, is both complicated and uncertain. It

consists in extracting the coffee-beans with water, precipitating the tannic acid from the solution by lead-salts, and evaporating only the solution freed from lead for crystallization. This method is exceedingly inconvenient, and this is probably the principal reason why the statements as to the amount of caffeine in coffee differ so much from each other.

The following method appears to the author to be much simpler and to lead to more accurate results. It is founded on the treatment of powdered coffee-beans with commercial benzole. This extracts two constituents from the coffee—oil of coffee and caffeine. After the evaporation of the benzole, these two substances may be easily separated from each other by agitation with hot water, in which the caffeine dissolves, whilst the oil floats on the surface and may be skimmed off. The caffeine is obtained by the evaporation of the aqueous solution, in very beautiful crystals, which may be sublimed.

The whole of the benzole may be recovered, by distilling it in a retort, after it has stood about a week upon the coffee-beans. The residue in the retort is the oil of coffee and caffeine, which may be separated as above by agitation with water, or by treatment with æther, which dissolves the oil and leaves the caffeine in crystals. By this method oil of coffee and caffeine might be obtained as subsidiary products in benzole manufactories.—*Kunst- und Gewerbeblatt für Bayern*, 1858, p. 27.

On the Arsenio-methylic Compounds. *By* A. Bäyer.

The author first calls attention to the fact that in the consideration of the arseniferous organic compounds, it has of late been the custom to notice principally those conditions which stand in intimate connexion with the nitrogen group, and to neglect more or less those caused by the individual difference of the arsenic. He has set himself the task of filling up this gap in our knowledge, by studying those arsenical compounds to which no corresponding nitrogenous compounds are known.

Cacodyle was selected as the starting-point of the investigation, as this, of all arsenical substances, had presented the greatest difficulties in a systematic point of view. The author started from the action of pentachloride of phosphorus upon cacodylic acid, which took place in accordance with the following equation:—

$$\underset{\text{Cacodylic acid.}}{As\,(C^2\,H^3)^2\,HO^4} + 2PCl^5 = \underset{\text{Terchloride of cacodyle.}}{As\,(C^2\,H^3)^2\,Cl^3} + 2PO^2\,Cl^3 + HCl.$$

The terchloride of cacodyle thus formed, which may also be obtained by the direct action of chlorine upon chloride of cacodyle, is a colourless substance which crystallizes in columns from æther; when heated it is decomposed into protochloride of methyle and perchloride of arsenio-monomethyle:—

$$As\,(C^2\,H^3)^2\,Cl^3 = As\,(C^2\,H^3)\,Cl^2 + C^2\,H^3\,Cl\,;$$

it is also converted by moisture into basic superchloride of cacodyle. The formation of terchloride of cacodyle from cacodylic acid and of

basic superchloride of cacodyle from the former, permitted some conclusions to be drawn as to the nature of cacodylic acid. Thus as pentachloride of phosphorus can only replace the oxygen of the type by chlorine, cacodylic acid must have the formula

$$As \left\{ \begin{matrix} (C^2 H^3)^2 \\ H \end{matrix} \right\} O^4,$$

by which means it becomes comparable with metaphosphoric acid, and the terchloride of cacodyle with oxychloride of phosphorus. Basic superchloride of cacodyle must in this point of view be regarded as belonging to an intermediate type; its analogue is to be found in Berthelot's monochlorhydrine. A compound corresponding with dichlorhydrine could not be obtained; the continued action of muriatic acid upon cacodylic acid furnished the above-mentioned product of the decomposition of terchloride of cacodyle, bichloride of arsenio-monomethyle:—

$$As (C^2 H^3)^2 HO^4 + 3HCl = As (C^2 H^3) Cl^2 + 2H^2 O^2 + C^2 H^3 Cl.$$

It is remarkable that this chloride possesses the same boiling-point as chloride of arsenic, and exerts a terrible action on the mucous membranes. It combines, like chloride of cacodyle, with chlorine, and forms tetrachloride of arsenio-monomethyle. This last substance, however, can only be obtained in a freezing mixture; it is decomposed, even near the freezing-point, into protochloride of methyle and chloride of arsenic. Bromine gives a corresponding series of reactions.

The series of processes which rendered it possible to descend from chloride of cacodyle to chloride of arsenic, and to replace one methyle after the other by chlorine, may also be traced upwards in the higher methylated compounds of arsenic. These conditions are elucidated by the following Table:—

As	$C^2 H^3$	$C^2 H^3$	$C^2 H^3$	$C^2 H^3$	Cl						
						As	$C^2 H^3$	$C^2 H^3$	$C^2 H^3$	$C^2 H^3$	
As	$C^2 H^3$	$C^2 H^3$	$C^2 H^3$	$C^2 H^3$	Cl	Cl					
						As	$C^2 H^3$	$C^2 H^3$	$C^2 H^3$	Cl	
As	$C^2 H^3$	$C^2 H^3$	$C^2 H^3$	Cl	Cl	Cl					
						As	$C^2 H^3$	Cl	Cl		
As	$C^2 H^3$	Cl	Cl	Cl	Cl						
						As	Cl	Cl	Cl		

The author believes that the same series would also be demonstrable in the other elements of the nitrogen group, antimony, bismuth, and phosphorus, and only expresses some doubts with regard to nitrogen, because this element has but little affinity for chlorine.

Those arsenical compounds which are brought together in the above Table, and which may be regarded as the starting-point for all arsenio-methylic compounds, evidently fall into two groups. One of these corresponds with the type ammonia, and the other with that of chloride of ammonium. Both in their physical properties and in the reactions produced by the compounds which follow each other, this agreement is most distinctly shown.

The author also calls attention to the fact that similar series are known in other departments of organic chemistry. Olefiant gas,

for example, exhibits an exactly similar behaviour towards chlorine, and by the alternate action of chlorine and alcoholic solution of potash upon it one atom of hydrogen after the other may be replaced by chlorine, as is the case with the methyle in the arsenical compounds. The consideration of these series is recognized as an essential means of advancing the theoretical views upon organic bodies, as by this means the mutual relations of non-homologous radicals is explained. It was specially shown in the arsenic series, that each member of this, by its action upon bodies of another type and contrasting properties, produced groups of compounds containing radicals the basicity of which is expressed by the number of atoms of chlorine which are combined with them in the principal series. In this way compounds may be derived from bichloride of arsenio-tetramethylium, in which the arsenio-tetramethylium displaces 1 atom of hydrogen, whilst arsenio-trimethyle always behaves as a bibasic radical. Cacodyle in chloride of cacodyle again is monobasic; on the other hand, the substances derived from terchloride of cacodyle contain the same radical in the place of 3 atoms of hydrogen, as has already been shown. To prove this regularity throughout, it only remained to be shown that the bodies which may be prepared from bichloride of arsenio-monomethyle contain monomethyle as a bibasic radical, and that there are compounds in which the same atomic group occurs as tetrabasic. As a proof of this, a number of compounds of arsenio-monomethyle are described. All substances derived from the bichloride contain 2 atoms of sulphur, iodine, or oxygen to 1 atom of arsenic, and arsenio-monomethylic acid may be regarded as a compound of the tetrabasic radical arsenio-monomethyle.—*Verhandl. des naturhist.-medic. Vereins zu Heidelberg*, March 1, 1858.

On a Modification of Mohr's *Alkalimeter. By* J. W. Slater*.

Mohr's pourette or alkalimeter, although very convenient for use, is open to some objections. The caoutchouc tube through which the test-liquor flows is affected by certain reagents, *e. g.* the permanganate of potash; the spring-clip which regulates the flow of the liquid is injured by the fumes, and a variable quantity of the test-liquid is retained by capillary attraction in the delivery-tube below the clip. To obviate these disadvantages, I propose the following modification. The pourette terminates below in a finely drawn out delivery-tube, and is provided at the top with two orifices, as in the alkalimeter of Binks. One of these is provided with a well-fitting ground glass stopper, and to the other is fixed a piece of vulcanized tubing furnished with a spring-clip. To fill this instrument, the aperture below is closed with a pellet of wax, or with the finger, and the glass stopper withdrawn. When full, the stopper is replaced, and the pourette suspended on its support. By pressing the clip, air is admitted above, and the test-liquid allowed to flow out drop by drop from the delivery-aperture.

* Communicated by the Author.

PROCEEDINGS OF SOCIETIES.

Royal Society.

April 29, 1858. (J. P. Gassiot, Esq., Vice-President, in the Chair.)

"Note on the Measurement of Gases in Analysis." By A. W. Williamson, Ph.D., F.R.S., Professor of Chemistry in University College, and W. J. Russell, Ph.D.

In Bunsen's admirable method of gas analysis, considerable time and trouble are expended in observing the exact temperature and pressure to which the gas is subjected at the time of measurement; and also in calculating from these data the volume which the gas would occupy at the normal temperature and pressure. Frankland's excellent apparatus, on the other hand, protects the gas from the influence of variations of atmospheric pressure, and, under favourable conditions, even from the influence of change of temperature; but the complication of this apparatus, and its liability to derangement, seem likely somewhat to limit its use.

If, when a fall of temperature takes place, we could diminish the pressure on the gas exactly in proportion to the diminution of elasticity which it undergoes, such fall of temperature would evidently not alter the volume of gas in the eudiometer. In like manner a rise of temperature might, if known, be counteracted by lowering the eudiometer-tube. The same remarks apply to variations of barometric pressure; as an increase of this influence might be counterbalanced by raising the eudiometer, and a diminution by depressing it.

It is therefore a question of some interest to find, for any atmospheric temperature and pressure, at what height of the eudiometer the enclosed gas will occupy the same volume as at the normal temperature and pressure. This is easily found by introducing a standard quantity of air into a tube over mercury, marking off the height of the mercury in the tube at the normal temperature and pressure; then, at any other temperature or pressure, raising or lowering the tube in the mercurial trough so as exactly to bring the enclosed air to its normal volume. The mercurial pressure needed for this purpose is evidently the same as that needed under the same circumstances for the reduction of any quantity of gas to the volume which it would occupy at the normal temperature and pressure.

The apparatus we use in applying this principle to gas analysis (fig. 1) consists essentially of the ordinary Bunsen's eudiometer, and a "pressure-tube," which is simply a tube of some 6 or 7 inches in length, and about the diameter of an ordinary eudiometer. It is closed at one end, and to the other is fixed a smaller tube of about the same length. Such a quantity of air is introduced into this pressure-tube, that when it is inverted in the trough the mercury stands at a convenient height in the narrow tube. At this point a mark is made, which indicates the height of mercury needed at any temperature or pressure to reduce the enclosed air to its original volume. The mercurial trough which we have used differs only

from the ordinary one in being provided with a well at one end, thus enabling the operator to raise or depress the eudiometer at pleasure, so as always to bring the gas which it contains to the same pressure as the air in the pressure-tube. Both the eudiometer and the pressure-tube are held in a perpendicular position by means of clamps which slide on upright rods. Each clamp is provided with a simple kind of slow movement, by which the tube can be raised or lowered by the operator whilst he is looking through a horizontal telescope at a suitable distance. We place the pressure-tube in front of the eudiometer, and by means of the fine adjustment bring the column of mercury in the small tube exactly to the normal mark. The eudiometer is then adjusted, also by means of the slow movement, so that the top of its meniscus (as seen through the horizontal telescope) exactly coincides with the top of the meniscus in the pressure-tube. This is easily done; for the diameter of the pressure-tube is considerably smaller than that of the eudiometer, and the meniscus in the latter can be clearly seen on both sides of the meniscus in the pressure-tube.

By this method we are able to obtain very accurate results with considerably less trouble than by Bunsen's method, and also without having any calculations to perform. The following analyses made during very stormy weather, of air deprived of its carbonic acid by potash, gave results amongst which the greatest difference was only four hundredths of a per cent. (·04).

I.

Volume of air taken		144·81
After addition of hydrogen		234·50
After explosion		144·00
Nitrogen	79·168	
Oxygen	20·832	
	100·000	

II.

Volume of air taken		139·55
After addition of hydrogen		229·07
After explosion		141·89
Nitrogen	79·176	
Oxygen	20·824	
	100·000	

III.

Volume of air taken		148·1
After addition of hydrogen		236·04
After explosion		143·30
Nitrogen	79·139	
Oxygen	20·861	
	100·000	

Fig. 1.

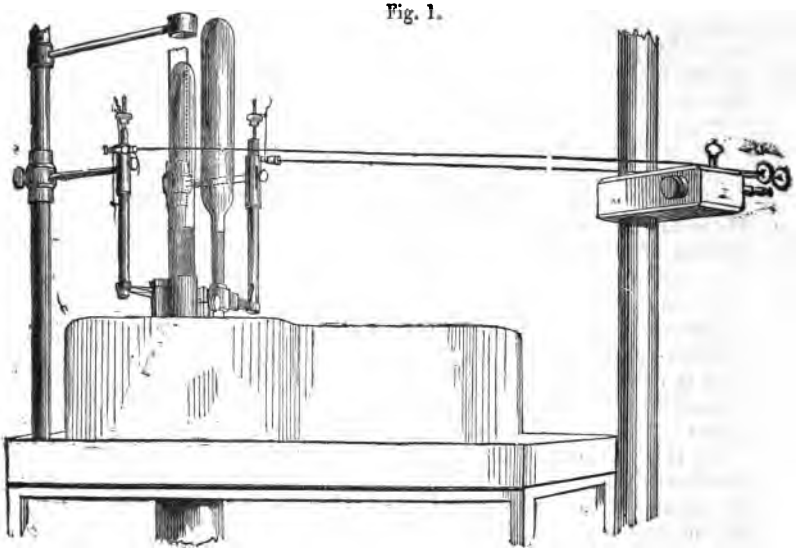
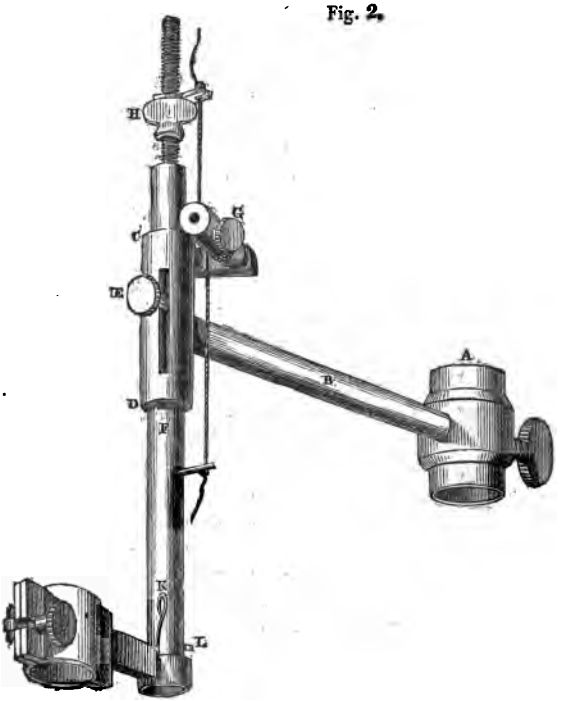


Fig. 2.



IV.

Volume of air taken	149·14
After addition of hydrogen . .	248·57
After explosion	155·28
Nitrogen . . .	79·150
Oxygen. . . .	20·850
	100·000

We are still engaged in experiments on this and some other points of gas analysis, and hope to have the honour of communicating our results before long.

DESCRIPTION OF THE FIGURES.

Fig. 1 represents the whole apparatus.

Fig. 2 represents the clamp with the fine adjustment attached to it.

A is the part which slides up and down the vertical rod; it is furnished on the inside with a small steel peg which moves in a groove, thus causing this arm always to remain in the same plane.

C D is a tube through which the rod F carrying the clamp passes.

E is a screw which retains the rod F in its place, and by means of which the friction of the rod passing through the tube can be increased.

G is the fine adjustment. As this small cylinder is turned round to the right or to the left, so the string either above or below it is wound on to it, and consequently the rod F raised or lowered.

H is merely an arrangement by which the string can always be tightened.

K is a peg so placed with regard to the stop L, that when, by turning the clamp round, it is pressed against the stop, the tube is then in the right position for applying the final adjustment and reading off.

May 6. (The Lord Wrottesley, President, in the Chair.)

"Notes of Researches on the Poly-Ammonias." By A. W. Hofmann, LL.D., F.R.S.—No. II. Action of Chloroform upon Aniline.

In a former Note I have alluded to some new alkaloids which are produced by the action of the bromides of triatomic alcohols upon the primary amidogen bases.

I have since examined more minutely one of these bodies. At the common temperature, chloroform and aniline may be left in contact for a considerable time without any change becoming perceptible. Even at the temperature of boiling water scarcely any reaction takes place. But on exposing for ten or twelve hours a mixture of about equal volumes of chloroform and aniline in sealed tubes to a temperature of 180° or 190° C., a hard brown crystalline mass is obtained, which consists chiefly of the hydrochlorates of aniline and of a new crystalline base.

To obtain this compound in a state of purity, the brown crystalline mixture formed in the digester-tubes is triturated with a small quantity of water, thrown upon a filter and washed with water. The first washings chiefly consist of hydrochlorate of aniline, which base separates in oily globules on addition of potassa to the filtrate. By testing the filtrate in this manner from time to time, it is found that the basic body separated by addition of potassa gradually exhibits a tendency to solidify, and ultimately falls as a yellowish-white crystalline precipitate. The residue upon the filter is now dissolved in warm (not boiling) water, separated by a filter from a brown resinous

insoluble substance, and precipitated by ammonia or potassa. The crystalline precipitate obtained in this manner is washed till free from alkali, and repeatedly crystallized from weak spirit. It is difficult to obtain it perfectly white, a yellowish substance, which appears to be partly formed during the process of solution, adhering with great pertinacity.

Thus obtained, the new base is a white crystalline powder; frequently it is obtained in minute scales, generally of a yellowish tint. It is insoluble in water, but readily dissolves in alcohol and ether. From the hot solution in these solvents it is precipitated by water as a yellow oil, solidifying on cooling with crystalline structure. It is easily dissolved by acids, with many of which it forms crystalline compounds. From the saline solutions thus produced the base is reprecipitated by potassa and also by ammonia. The salts of the new base are not very stable; their solutions, especially when heated for some time, inevitably contain more or less aniline, the crystalline base itself undergoing changes which I have not yet sufficiently examined.

The analysis of the new compound presents some difficulty. Even after protracted exposure over sulphuric acid in the exsiccator, it retains a small quantity of water, while a temperature of 100° is apt to decompose it.

The nature of the body was, however, readily established by the examination of a perfectly stable hydrochlorate, and also of a very definite platinum-salt.

The results obtained in the analysis of these salts establish for the new base the formula

$$C_{26}H_{12}N_2 = \left.\begin{matrix}(C_{12}H_5)_2\\(C_2\,H)'''\\H\end{matrix}\right\} N_2.$$

It is obviously formed by the substitution of the triatomic molecule $(C_2H)'''$ for 3 equivalents of hydrogen in 2 molecules of aniline, which thus coalesce into a diamine molecule. Accordingly the base might be called diphenyl-formyl-diamine, that is, diammonia, in which 2 equivalents of hydrogen are replaced by 2 molecules of phenyle, and 3 equivalents of hydrogen by 1 molecule of formyle, 1 equivalent of hydrogen remaining unreplaced. Its formation is expressed by the equation

$$\underbrace{4(C_{12}H_7N)}_{\text{Phenylamine aniline.}} + \underbrace{C_2HCl_3}_{\text{Terchloride of formyle (chloroform).}} = \underbrace{C_{26}H_{12}N_2HCl}_{\text{Hydrochlorate of diphenyle-formyle-diamine.}} + \underbrace{2(C_{12}H_7N_1HCl)}_{\text{Hydrochlorate of phenylamine.}}$$

As seen from this equation, the new base, although unmistakeably corresponding to 2 molecules of ammonia, like many other polyammonias, is monoacid.

The analysis of the hydrochlorate leads in fact to the formula

$$C_{26}H_{12}N_2, HCl.$$

The platinum-salt contains

$$C_{26}H_{12}N_2, HCl, PtCl_2.$$

The new derivative of aniline undergoes several remarkable changes which require further elucidation.

THE CHEMICAL GAZETTE.

No. CCCLXXVIII.—July 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Formation of Glycolic Acid from Acetic Acid.
By M. KEKULÉ.

IN his investigation of monochloracetic acid, lately carried on in the author's laboratory, R. Hoffmann observed a peculiar decomposition of the monochloracetates, in which metallic chloride and an acid were produced, without the formation of any third product being observed. Hoffmann arrived at no definite results as to the nature of this acid, but expressed the opinion that it might be glycolic acid. The theoretical importance of this formation of an acid with a biatomic radical, from a monobasic acid, gave origin to a new investigation, by which the supposition put forward by Hoffmann was confirmed.

The author first indicates why he regards this decomposition as particularly interesting in a theoretical point of view.

Alcohol. $\left.\begin{matrix} C^4H^5 \\ H \end{matrix}\right\} O^2$ Acetic acid. $\left.\begin{matrix} C^4H^3O^2 \\ H \end{matrix}\right\} O^2.$

Glycol. $\left.\begin{matrix} C^4H^4 \\ H^2 \end{matrix}\right\} O^4$ Glycolic acid. $\left.\begin{matrix} C^4H^2O^2 \\ H^2 \end{matrix}\right\} O^4.$

From the monoatomic alcohols Wurtz has recently obtained a remarkable group of bodies, the glycols. Every alcohol corresponds with a glycol; the monoatomic radical of the alcohol becomes the biatomic radical of the glycol by the loss of 1 atom of hydrogen. Every alcohol also corresponds with an acid (*e. g.* acetic acid), which belongs to the same type, H^2O^2, only contains O^2 in place of H^2 in the radical, and may be obtained from the corresponding alcohol by oxidation. In the same way every glycol corresponds with a bibasic acid, in the formation of which also 2 atoms H of the radical are replaced by O; and Wurtz has actually shown that glycolic acid is obtained by oxidation from glycol, but that the next

member of the homologous series, propyloglycol, $C^6 \left.\begin{matrix} H^6 \\ H^2 \end{matrix}\right\} O^4$, furnishes lactic acid, $\left.\begin{matrix} C^6 H^4 O^2 \\ H^2 \end{matrix}\right\} O^4$. From the monoatomic alcohols, therefore, biatomic glycols may be obtained; acids are produced from both by oxidation; the recent formation of glycolic acid from acetic acid now shows, as regards the two groups of acids, the same thing that was proved by Wurtz with respect to the two classes of alcohols.

The reaction is, however, particularly interesting also, because the conversion of the monoatomic radical of acetic acid into the biatomic radical of glycolic acid may be traced completely; and because it is distinctly seen that this conversion takes place by elimination of chlorine, and therefore by the indirect elimination of one atom of hydrogen.

If we now, as must be the case from these considerations, assume the formulas of glycolic and lactic acids as half what has hitherto been admitted, these acids appear to be homologous with carbonic acid. The bodies hitherto regarded as amides (the acids written with double formulæ), glycocoll, alanine, &c., appear to be aminic acids; the so-called acid salts of lactic acid become hyperacid salts, corresponding with the acid salts of acetic acid, and the quadroxalate of potash. That glycolic acid with the formula $\left.\begin{matrix} C^4 H^2 O^2 \\ H^2 \end{matrix}\right\} O^4$ contains two atoms of hydrogen outside the radical, is shown by the existence of benzoglycolic acid; it is only remarkable that of these two atoms of hydrogen only one is displaceable by metals, whilst in the homologous carbonic acid both atoms of hydrogen are displaced by metals with equal facility; the author promises to put forward a view of the molecular constitution of the chemical compounds, from which this difference of substances so nearly allied and belonging to the same homologous series may be derived.

The new mode of formation of glycolic acid, moreover, furnishes further experimental data for the systematic arrangement of organic compounds, which the author has long used in his lectures, and the leading idea of which he represents by the following scheme:—

	Group 1.	Group 2.	
Monoatomic radicals	$C^2 H^3$	$C^2 HO^2$	
	$C^4 H^5$	$C^4 H^3 O^2$	
	$C^6 H^7$	$C^6 H^5 O^2$	
	Group 3.	**Group 4.**	**Group 5.**
Biatomic radicals	$C^2 H^2$	$C^2 O^2$	..
	$C^4 H^4$	$C^4 H^2 O^2$	$C^4 O^4$
	$C^6 H^6$	$C^4 H^4 O^2$	..
	$C^8 H^8$	..	$C^8 H^4 O^4$
	Group 6.	**Group 7.**	
Triatomic radicals (also monoatomic)	$C^2 H$	..	
	$C^4 H^3$	$C^4 HO^2$	
	$C^6 H^5$	$C^6 H^3 O^2$	

The mode of arrangement is intelligible from the preceding:—

biatomic radicals are produced from monoatomic radicals by loss of H; by the further elimination of hydrogen the triatomic radicals are produced; on the other hand, by the admission into the radical of oxygen in place of hydrogen, acid radicals are produced.

Group 1. Includes the alcohols and all their derivatives.
„ 2. „ the fatty acids.
„ 3. „ Homologues of elayle, glycols, &c.
„ 4. „ Carbonic acid, glycolic acid, lactic acid, &c.
„ 5. „ Oxalic acid, succinic acid, &c.
„ 6. „ Chloroform, glycerine, &c., and also allylic alcohol, &c.
„ 7. „ Acroleine, acrylic acid, &c.

The conversion of monochloracetic acid takes place with wonderful facility when the monochloracetates are heated. Crystallized, air-dried monochloracetate of potash, furnishes in this way both glycolic acid and glycolide, in accordance with the equation

$$\left.\begin{matrix} C^4 H^2 ClO^2 \\ K \end{matrix}\right\} O^2 = KCl + C^4 H^2 O^3 . O^2,$$

but glycolic acid always predominates, because the potash-salt undergoes decomposition before it has lost its water of crystallization. The best mode is to heat a concentrated aqueous solution of monochloracetate of potash in a closed apparatus to 248° F., evaporate it to dryness, and extract it with a mixture of alcohol and æther. On evaporating this solution, the glycolic acid remains as an uncrystallizable mass; but if it be separated from the silver-salt by sulphuretted hydrogen, or from the lime-salt by sulphuric acid, it may be easily obtained crystallized. The lime-salt and the silver-salt were analysed; the baryta-salt and the lead-salt were also prepared. From the observed properties of these compounds, the author comes to the conclusion that all the glycolic acids prepared by previous observers (Socoloff, Strecker, Cloez, Dessaignes, Debus, Wurtz) by other reactions are identical, and that there are not, as has been asserted, two modifications of this acid.

Monochloracetate of ammonia is decomposed exactly in the same way as the potash-salt; it furnishes muriate of ammonia and glycolic acid,

$$C^4 H^3 Cl (H^4 N) O^4 + H^2 O^2 = C^4 H^4 O^6 + NH^4 Cl,$$

whilst glycocoll might possibly have been produced:—

$$C^4 H^2 Cl (H^4 N) O^4 = C^4 H^5 NO^4 + HCl.$$

The aromatic acids appear to exhibit a different behaviour; at least no oxybenzoic acid could be obtained by heating monochlorobenzoic acid.— *Verhandl. des naturhist.-medic. Vereins zu Heidelberg*, February 8, 1858.

On the Behaviour of Boron to Nitric Oxide. *By* Prof. Wöhler.

From the remarkable affinity between nitrogen and boron*, it was worth while to examine how the latter would behave when heated

* Liebig's Annalen, cv. p. 69.

in nitric oxide gas. It appeared that amorphous boron, when heated not quite to redness in a current of dried nitrous gas, ignited and burnt with a most dazzling incandescence. The product is gray, and consists of a mixture of boracic acid and nitruret of boron, coloured by some intermixed, unaltered boron. The latter and the boracic acid may be extracted by water and nitric acid. The nitruret of boron thus formed has all the properties of that prepared in other ways; with fusing hydrate of potash it evolves a great quantity of ammonia. In this case therefore both elements of the nitric oxide are combined by the boron. 5 equivs. of boron form with 3 equivs. of nitric oxide, 2 equivs. of boracic acid and 3 equivs. of nitruret of boron. The two crystallized modifications of boron do not decompose nitric oxide, at least not at a red heat which is resisted by a glass bulb.—Liebig's *Annalen*, February, 1858, p. 259.

On the Oxalates of the Oxides of the Heavy Metals.
By A. Souchay *and* E. Lenssen.

Oxalate of Bismuth, $(BiO^3)^2, 3C^4O^6+15HO$, is produced when a saturated solution of oxalic acid is mixed with a clear solution of nitrate of bismuth. At 212° F. it loses 13 atoms of water, and has then the formula $(BiO^3)^2, 3C^4O^6+2HO$; at a higher temperature it is decomposed, becomes reddish brown, dark brown, and black, and then consists of a mixture of oxalate of bismuth and suboxide of bismuth ($BiO^2=224$). It is a crystalline precipitate of a dazzling white colour, and contains 56·67, 56·95, and 56·67 per cent. of BiO^3 (calculated 56·97). The salt is insoluble in water; when left long in contact with water it is decomposed, oxalic acid being dissolved, whilst basic oxalate of bismuth is left. It is difficult of solution in cold nitric acid, but dissolves readily in that fluid when heated. It dissolves readily in muriatic acid even in the cold; is insoluble in alcohol and æther; dissolves with difficulty in acetic and oxalic acids.

Oxalate of Bismuth and Potash, $\left.\begin{matrix}BiO^3\\3KO\end{matrix}\right\}3C^4O^6+2\left.\begin{matrix}KO\\KO\end{matrix}\right\}C^4O^6+24HO$, is produced when neutral oxalate of bismuth is put into a hot solution of normal oxalate of potash. The oxalate of bismuth dissolves, and the solution, which is nearly saturated, is filtered. The salt crystallizes in small columnar crystals. It gave 28·12 per cent. of potash and 20·45 per cent. of oxide of bismuth. Its mother-liquor furnishes another salt of the composition $\left.\begin{matrix}BiO^3\\3KO\end{matrix}\right\}3C^4O^6+4\left.\begin{matrix}KO\\KO\end{matrix}\right\}C^4O^6+24HO$. This salt is decomposed by water into basic oxalate of bismuth and oxalate of potash which dissolves.

Oxalate of Bismuth and Ammonia, $\left.\begin{matrix}BiO^3\\3NH^4O\end{matrix}\right\}3C^4O^6+6\left.\begin{matrix}NH^4O\\NH^4O\end{matrix}\right\}C^4O^6+24HO$.—Normal oxalate of bismuth is added to a hot solution of oxalate of ammonia, as long as it dissolves; the liquid is then filtered and left to crystallize. It gave 42·66 per cent. of

oxalic acid, 15·92 of oxide of bismuth, and 25·92 of ammonia. It dissolves in hot water; crystallized oxalate of bismuth soon separates from this solution.

Basic Oxalate of Bismuth is formed when the neutral salt is repeatedly boiled with water. Heintz found its composition to be $2BiO^3 + 2C^4O^6 + 2HO$. The authors found 72·39 per cent. of oxide of bismuth, which agrees better with the formula $BiO^3, C^4O^6 + 2HO$. At 212° F. it lost no water, and was decomposed at 270° F. It is difficult of solution in acetic and oxalic acids, but readily soluble in nitric and muriatic acids.

Oxalate of Antimony.—The authors did not succeed in obtaining the neutral salt. They always obtained the basic salt, which corresponds with the preceding salt of bismuth and had already been prepared by Peligot. Its formula is $SbO^3, C^4O^6 + 2HO$. A solution of protochloride of antimony in muriatic acid is added to a cold saturated solution of oxalic acid, and the clear mixture is left standing for about 24 hours. In the course of this time the salt separates as a granular precipitate. Under the microscope this is found to consist of white globular masses. Oxalate of antimony loses a part of its oxalic acid, and becomes still more basic by boiling with water. When dried at 212° F. it loses 1 equiv. of water; at 428° F. it becomes anhydrous, but decomposition commences at the same time. The salt becomes blackish, probably from the formation of suboxide of antimony. It gave 61·14 per cent. SbO^3 and 31·33 of oxalic acid.

Oxalate of Antimony and Potash, $\left.\begin{matrix}SbO^3\\3KO\end{matrix}\right\} 3C^4O^6 + 12HO$, is obtained when oxide of antimony prepared in the humid way is put into a tolerably concentrated solution of binoxalate of potash; the solution is filtered and left to crystallize. It forms wart-like aggregations, which appear under the microscope as beautifully clear columnar crystals, adhering together in tufts.

It dissolves in water without decomposition. According as more or less of a mineral acid is added, the salt is decomposed, so that either oxalic acid or basic oxalate of antimony separates. The salt has an acid reaction. It is insoluble in æther, but somewhat soluble in alcohol. When dried at 212° F., it lost 6 equivs. of water. It gave 23·10 and 23·84 per cent. SbO^3.

Oxalate of Antimony and Soda, $\left.\begin{matrix}SbO^3\\3NaO\end{matrix}\right\} 3C^4O^6 + \left.\begin{matrix}NaO\\NaO\end{matrix}\right\} C^4O^6 + 20HO$, was obtained in the same way as the potash double salt. It forms well-developed crystals, which when dried at 212° F. lost 10 equivs. of water. They contained 18·63 per cent. SbO^3 and 19·88 of soda.

Oxalate of Antimony and Ammonia, $\left.\begin{matrix}SbO^3\\3NH^4O\end{matrix}\right\} 3C^4O^6 + 4HO$, was obtained by dissolving oxide of antimony in a hot concentrated solution of oxalate of ammonia. By evaporation and refrigeration, the solution became thick, but furnished no crystals. Precipitation by absolute alcohol gave first a voluminous precipitate of oxalate

of ammonia, and afterwards, when three times the volume of alcohol had been added, the salt separated in needles. It gave 29·89 and 30·23 per cent. of SbO^3, 45·87 per cent. C^4O^6, and 15·87 per cent. of ammonia (NH^4O).

Oxalate of Manganese and Potash, $\left.\begin{matrix}Mn^2O^3\\3KO\end{matrix}\right\}3C^4O^6+6HO$.—When artificial peroxide of manganese is agitated with a solution of oxalic acid, it furnishes a solution of peroxalate of manganese which soon becomes converted into protosalt. If the solution of 3 parts of oxalic acid be neutralized with carbonate of potash, and 4 parts of oxalic acid be added to it, before the artificial peroxide of manganese is put in, the fluid being left somewhat acid, the oxide of manganese dissolves with effervescence. A fluid of a beautiful purple-red colour is obtained, but this is very easily decomposed. An exposure of a few seconds to clear daylight is sufficient to decompose it immediately with effervescence. Its temperature must also be kept below 32° F., if it is to be preserved at all. It is obtained in needles of a fine purple-red colour, when the solution is mixed with absolute alcohol, whilst it is refrigerated and kept from the light.

Protoxalate of Iron, $\left.\begin{matrix}FeO\\FeO\end{matrix}\right\}C^4O^6+4HO$.—Protosulphate of iron is dissolved and mixed with half its weight of oxalic acid. The salt separates as a citron-yellow powder. It dissolves in 4500 parts of cold and 3800 parts of hot water.

Protoxalate of Iron and Potash, $\left.\begin{matrix}KO\\FeO\end{matrix}\right\}C^4O^6+2HO$.—The preceding salt is dissolved abundantly by a hot solution of oxalate of potash. The fluid becomes deep yellow. It is separated by the addition of alcohol. Oily drops are thrown down, which afterwards solidify to a yellow mass. It contained 27·10 and 27·21 per cent. of potash.

Oxalate of Arsenious Acid and Potash, $\left.\begin{matrix}AsO^3\\3KO\end{matrix}\right\}3C^4O^6+6HO$, is obtained when arsenious acid is dissolved in a solution of binoxalate of potash. It forms beautiful hard crystals, which contained 20·47 AsO^3 and 25·94 KO.

Protoxalate of Platinum and Soda, $\left.\begin{matrix}PtO\\NaO\end{matrix}\right\}C^4O^6+4HO$, is obtained when oxide of platinum and soda is treated with oxalic acid; the oxide of platinum is reduced to protoxide with effervescence. The fluid produced exhibits the most remarkable phænomena of colour; it is at first red, and the colour then passes gradually to violet, and finally to deep indigo-blue. From this solution dark copper-red needles first of all separate; their composition is $\left.\begin{matrix}PtO\\NaO\end{matrix}\right\}C^4O^6+4HO$. Döbereiner regarded this salt as protoxalate of platinum. The subsequent crystallizations contain more soda. The salt does not remain undecomposed when exposed to the air, as long as it is in contact with water. When heated it detonates

slightly. It is but sparingly soluble in cold water, but dissolves in hot water with a greenish colour. This solution, when evaporated, becomes deep blue. Muriatic acid immediately destroys this colour. The salt is insoluble in æther and alcohol.—Liebig's *Annalen*, cv. p. 245.

On the Constitution of Aldehyde and Protochloride of Elayle.
By Dr. Anton Geuther.

Oxide of silver has no action upon chloride of elayle at a boiling heat. When sealed up in tubes and heated to 248° F., a partial decomposition took place. On opening the tube, it is found that there is a strong pressure in the interior; when the point is filed round it springs off with a violent report, the fluid contained in the tube disappears immediately, and the alliaceous odour indicates the formation of the compound $C^4 H^3 Cl$. The oxide of silver which remains in the tube contains a considerable quantity of chloride of silver.

The author attempted to decompose protochloride of elayle with potash. At 266°—284° F. all the tubes exploded. After heating them for several hours to 257° F., a fluid was formed of exactly the same properties as by the treatment with oxide of silver; on opening the point of the tube, there was explosion and disappearance of the fluid, and an alliaceous odour. The residue contained potash and chloride of potassium.

Neither oxide of silver nor potash, therefore, are capable of extracting the chlorine from protochloride of elayle, and replacing it by oxygen. The author now endeavoured to extract the oxygen from aldehyde and replace it by chlorine, in order to try whether chloride of elayle would be produced in this way. Aldehyde acts violently upon perchloride of tin, $SnCl^2$, but only SnCl, not SnO^2, is formed. The author therefore treated aldehyde with perchloride of phosphorus, and obtained a limpid liquid with a boiling-point of 140° F., of a sweetish ætherial odour and taste, presenting an illusive resemblance to those of chloroform. Spec. grav. at 39°·8 F.=1·189. Analysis:—

C	..	24·44	4	24·24
H	..	4·47	4	4·04
Cl	71·55	..	2	71·71

Hence this body is isomeric with protochloride of elayle, but is distinguished from the latter by its boiling-point, which is 34° F. lower, by its smaller specific gravity, and by its behaviour to an alcoholic solution of potash. In the cold it is not decomposed by alcoholic solution of potash, and not without difficulty when heated. When sealed up in a tube with alcoholic solution of potash and heated for a long time in the water-bath, it furnished chloride of potassium and a volatile chloride, which was driven off by the heat of the hand, and burnt with a flame with a green margin. It should probably to be ranged in one series with protochloride of œnanthy-

lene, $C^{14} H^{14} Cl^2$, and protochloride of valeraldehyde, $C^{10} H^{10} Cl^2$, and would have a corresponding member in the benzoic acid series in chloride of benzole, $C^{14} H^6 Cl^2$.

Perhaps this body is therefore the true chloric æther of glycol, which Wurtz considers to be the protochloride of elayle. From the circumstance that oxygen has a different specific volume in aldehyde and in alcohol, to which Kopp has called attention, the author concludes that it must exist in a different combination in aldehyde than in alcohol. But as in the latter it is probably combined with hydrogen, it must in this case be combined with carbon; the rational formula of aldehyde would thus be $C^2 H^4$, $C^2 O^2$, according to which it appears to be a compound of carbonic oxide with marsh-gas. The rational formula of the chloride is then $C^2 H^4$, $C^2 Cl^2$, representing a compound of marsh-gas with monochloride of carbon. Protochloride of elayle would be—

$$\begin{matrix} C^4 H^2, HCl \\ HCl, \end{matrix}$$

that is the chloric alcohol of the hydrocarbon $C^4 H^2$ (vinilyle).

Ordinary alcohol.	Vinylic alcohol.	Protochloride of elayle.
$C^4 H^4, HO$	$C^4 H^2, HO$	$C^4 H^2, HCl$
HO	HO	$HCl.$

The so-called chloride of elayle produced from protochloride of elayle by an alcoholic solution of potash, might be regarded as hydrochlorate of vinilyle, $C^4 H^2, HCl$, analogous to hydrochlorate of elayle (chloride of æthyle), $C^4 H^4, HCl$.

The author, regarding aldehyde as a compound of $C^2 H^4$ with $C^2 O^2$, derives the bibasic alcohols therefrom in the following way: —the group $C^2 H^4$, $C^2 O^2$ occupies the same place in glycol which is occupied in alcohol by the group $C^4 H^4, HO$:—

Ordinary alcohol.	Glycolic alcohol.
$(C^4 H^4, HO)$	$(C^2 H^4, C^2 O^2)$
HO	$HO, \quad HO$

and the bibasicity follows necessarily from the bibasic nature of $(C^2 H^4, C^2 O^2)$:—

$$\begin{matrix} C^2 H^4 = 1\text{-basic}; & C^2 O^2 = 2\text{-basic, consequently} \\ 1 \quad + & 2(-1) = 2. \end{matrix}$$

The author considers it even probable that the aldehydes are the æthers of the bibasic alcohols. This opinion is supported by the fact that no other body could be prepared as the æther of glycol, as even benzolic alcohol always furnishes oil of bitter almonds when treated in such a way that it should furnish æther.

At the close of this memoir the author refers to the fact discovered by Kopp, that oxygen has two specific volumes in organic compounds (3·9 when in Gerhardt's types it is outside the radicals, 6·1 when it stands in the radicals; Kopp). The author details the reasons which lead him to think it probable that oxygen has the specific volume 3·9 when it is combined with hydrogen, whilst it has the volume 6·1 when combined with carbon. In water, in the

alcohols, and the simple æthers, where it is combined with hydrogen to form HO, it has the specific volume 3·9; in the aldehydes, where it is combined with carbon to form $C^2 O^2$, its specific volume is 6·1; in the acids it is combined partly with hydrogen and partly with carbon. In the fatty acids, 2 atoms of oxygen are combined with 2 atoms of hydrogen to form 2HO, and 2 atoms of oxygen with 2 atoms of carbon to form $C^2 O^2$. The author therefore writes formic acid, for example, $\left.\begin{matrix}HO\\HO\end{matrix}\right\} C^2 O^2$, and benzoic acid, $\left.\begin{matrix}C^{12} H^4, HO\\HO\end{matrix}\right\} C^2 O^2$, in which he starts from the principle of reducing all compounds into binary ones.—Liebig's *Annalen*, cv. p. 321.

On Iodide, Bromide, and Chloride of Aluminium. By M. Weber.

By heating iodine or iodide of silver with aluminium iodide of aluminium, AlI^3, is obtained. This compound is very easily decomposed, even at its melting-point. The vapour of iodide of aluminium burns with a beautiful orange-red flame. It dissolves in water with great evolution of heat; if the solution be evaporated over sulphuric acid, there remains hydrated iodide of aluminium, $Al^2 I^3 + 12HO$. This body is also produced when hydrated alumina is dissolved in hydriodic acid.

Iodide of aluminium forms a double salt with iodide of potassium, but apparently not with the other metallic iodides. In an atmosphere of dry ammonia it absorbs ammonia, falls into a snow-white powder, which contains at least 1 equiv. of ammonia, is insoluble in water, and when boiled with water is decomposed, depositing hydrated alumina and setting free ammonia.

Bromide of Aluminium, $Al^2 Br^3$, is produced by the careful treatment of aluminium with bromine. The combination takes place with incandescence. It fuses at 194° F., forming a limpid fluid, which boils at 509°—518° F. It is decomposed by the oxygen of the air when heated (like iodide of aluminium), so that it can only be obtained colourless by distillation over powder of aluminium. When sublimed, it forms aggregations of shining laminæ, more abundantly than the iodide.

Iodide and bromide of aluminium dissolve in sulphuret of carbon. The solutions fume in the air. By solution in water and evaporation to dryness, hydrated bromide of aluminium, $Al^2 Br^3, 12HO$, is obtained. Bromide of aluminium fuses with bromide of potassium into a double compound, $KBr + Al^2 Br^3$.

Bromide of aluminium absorbs ammonia and falls into a loose white powder; it loses the ammonia when heated, and reabsorbs it on cooling. It also absorbs sulphuretted hydrogen.

The author also prepared chloride of aluminium by the direct combination of chlorine and aluminium, in order to ascertain whether the colours attributed to chloride of aluminium are proper to that body, or due to impurities. Iodide and bromide of aluminium were also obtained coloured, but when carefully prepared with

an excess of aluminium, they were both colourless. The author heated chloride of aluminium in sealed tubes with powdered aluminium; under the pressure increased by the vapour he obtained it fluid, and after cooling snow-white.

Chloride of aluminium boils at 356°—365° F. (Liebig); bromide of aluminium at 509°—518° F.; iodide of aluminium above the boiling-point of mercury. The bromide is the most fusible; it melts under 212° F. All the three compounds dissolve in sulphuret of carbon; the chloride with most difficulty, the bromide most readily. The hydrates of all three contain 12 atoms of water.—Poggendorff's *Annalen*, ciii. p. 259.

On the Constitution of the Compounds of Stibæthyle and the Radicals of Stannæthyle. *By* A. Strecker.

According to the investigations of Löwig and Schweitzer, iodide of stibæthyle has 2 equivs. of iodine to $Sb(C^4H^5)^3$. In an investigation subsequently carried out in Löwig's laboratory, Merck obtained results from which he concluded that iodide of stibæthyle cannot have the formula $SbAe^3I^2$, but that it most probably contains 2 more equivs. of hydrogen. By the action of stibæthyle upon iodide of stibæthyle Merck obtained a compound crystallized in colourless octahedra, which contains only 1 equiv. of iodine to 1 equiv. of stibæthyle, and which is not converted into Löwig's iodide of stibæthyle by contact with iodine, but immediately forms that compound with hydriodic acid, and also instantly furnishes Löwig's chloride of stibæthyle by treatment with muriatic acid. With these octahedric crystals Merck obtained at the same time some more readily soluble crystals, which differed considerably in their form from the octahedric crystals. Merck gave them the formula $SbAe^3HI$, and explained the conversion by the equation

$$SbAe^3I^2H + SbAe^3 = SbAe^3I + SbAe^3IH.$$

The octahedric salt was also obtained by Merck, together with iodide of ammonium, by the action of ammonia upon Löwig's iodide of stibæthyle; he explained its formation by the equation

$$SbAe^3I^2H + NH^3 = SbAe^3I + NH^4I.$$

The author thought that Merck's octahedric compound contains 1 equiv. of oxygen, that it is in fact an oxyiodide. Its production from iodide of stibæthyle and aqueous ammonia is explained by the equation

$$\underset{\text{Iodide of stibæthyle.}}{SbAe^3I^2} + NH^3 + HO = \underset{\text{Oxyiodide of stibæthyle.}}{SbAe^3IO} + NH^4I.$$

The conversion of oxyiodide of stibæthyle into iodide of stibæthyle by hydriodic acid is equally simple,—

$$SbAe^3IO + IH = SbAe^3I^2 + HO.$$

To test this view the author mixed equal equivs. of iodide of stibæthyle and oxide of stibæthyle; he obtained the octahedric crystals,

and found in them 36·9 per cent. of iodine. This, like Merck's own results, agrees better with the composition $SbAe^3OI$. The production of this oxyiodide is therefore $SbAe^3O^2 + SbAe^3I^2 = 2SbAe^3OI$. The analyses are as follows:—

	Merck.			Strecker.				
Sb	..	..	..	..	..	1	120·3	35·1
C	20·7	20·7	20·6	..	..	12	72·0	21·0
H	4·5	4·5	4·6	..	..	15	15·0	4·4
I	37·1	36·9	36·8	37·7	36·9	1	127·0	37·1
O	..	..	..	..	..	1	8·0	2·3

The author further supposes that when Merck mixed stibæthyle with iodide of stibæthyle, the former was first converted into oxide, or moisture was attracted. There may then be formed—

$$SbAe^3 + SbAe^3I^2 + HO = SbAe^3HI + SbAe^3IO.$$

From the mixture, after the octahedric crystals of the oxyiodide had separated, Merck obtained other, more soluble crystals, which contained 36·5—36·8 per cent. of iodine, or less than the octahedric crystals. If these more soluble crystals contained water, and their composition were $SbAe^3HI + HO$, the amount of iodine would agree, as this formula requires 36·9 per cent. Consequently, the author concludes, all Merck's formulæ must undergo some change. The oxide prepared by Merck does not contain O, but O^2, and is identical with Löwig's oxide of stibæthyle. The composition of—

Neutral Sulphate of Stibæthyle is $SbAe^3O^2, HO, SO^3$ (Merck's formula is $SbAe^3O, SO^3$):—

	Calculated.		Found.
$SbAe^3O^2, HO$	232·3	85·3	..
SO^3	40·0	14·7	14·8

Neutral Nitrate of Stibæthyle is $SbAe^3O^2, HO, NO^5$ (Merck's formula, $SbAe^3O, NO^5$):—

	Calculated.		Found.
$SbAe^3O^2, HO$	232·3	81·1	..
NO^5	54·0	18·9	19·0

The chloride of stibæthyle of Merck, like his iodide, also contains 1 equiv. of oxygen.

The author at the same time remarks that it appears to him, that of the numerous stannæthyles obtained by Löwig, several are identical, and that the iodides described by him are also in part oxyiodides. The protiodide of methylene-stannæthyle, $Sn^2(C^4H^5)^2I$, is an oxyiodide of the formula $Sn^2(C^4H^5)^2IO$; the protiodide of elayle-stannæthyle $Sn^4(C^4H^5)^4I$ is also an oxyiodide of the formula $Sn^4(C^4H^5)^4IO^3$, so that stannæthyle, methylene-stannæthyle, and elayle-stannæthyle would be identical.

Of the other stannæthyles the author thinks, that as they exhibit such a variable proportion of tin and æthyle, they must be quite distinct from stannæthyle n (SnC^4H^5), nevertheless it is possible that the compounds of æthstannæthyle are double compounds of stannæthyle with methstannæthyle $[Sn^4(C^4H^5)^5 = Sn^2(C^4H^5)^3$

$+Sn^2(C^4H^5)^2$], and that the compounds of the former with halogens also contain oxygen. The compounds of acetstannæthyle might be double compounds of stannæthyle and a third radical $Sn^2C^4H^5$ ($Sn^4Ae^3+Sn^2Ae^2+Sn^2Ae$); thus, for example, iodide of acetstannæthyle, to which Löwig ascribes the formula Sn^4Ae^3I, is an oxyiodide of the formula $Sn^2Ae^2O^2+Sn^2AeI$. Consequently, three different stannic radicals would have to be assumed, namely,—

Radicals.	Iodides.	Corresponding inorganic compounds.
Sn^2Ae	$Sn^2Ae\ I$	Sn^2O^2
Sn^2Ae^2	$Sn^2Ae^2I^2$	Sn^2O^4
Sn^2Ae^3	Sn^2Ae^3I	Sn^2O^4.

All the compounds prepared by Löwig either contain these radicals, simply combined with iodine, bromine, oxygen, &c., or they are double compounds of two radicals.—Liebig's *Annalen*, cv. p. 306.

On Croton Oil. By Thomas Schlippe.

The author obtained the oil which he investigated by pressing the crushed seeds of *Croton Tiglium* between warm metal plates, after they had been warmed in the water-bath. The oil-cakes were then broken up small and extracted with alcohol of spec. grav. 0·848 in a displacement apparatus. It appeared that the alcohol did not dissolve the oil, but only displaced it. For the purpose of this extraction, the author employed an apparatus which enabled the alcohol flowing off to be distilled back again. After it had passed four times through the seeds, there were two strata in the receiver. The lower, oily one consisted of 14 parts of oil and 1 part of alcohol; the upper, which was thinly fluid, was composed of 23 parts of alcohol and 1 part of oil.

The seeds were pressed while still soaked with alcohol, by which means a considerable further quantity of oil was obtained; upon this a stratum of alcohol floated. From this third oil and the preceding the alcohol was distilled away, and the oil was then collected. The oil is thus obtained in four divisions:—

1. That pressed with the aid of heat;
2. That displaced by alcohol and retained in solution;
3. That displaced by alcohol and not dissolved, but obtained as an oily stratum below the preceding;
4. That expressed from the residue of 2.

The oils obtained by the different treatments of the seeds were of three kinds as regards their inflammatory action upon the skin. The most efficacious was that obtained from the alcoholic solution; whilst that which formed the thicker stratum below this solution was far less active; but the oils obtained by the first and second pressure were far inferior even to this in acridity.

The fatty oil of croton oil, when saponified, furnished stearic acid, $C^{36}H^{36}O^4$, palmitic acid, $C^{32}H^{32}O^4$, myristic acid, $C^{28}H^{28}O^4$, and lauric acid, $C^{24}H^{24}O^4$; of the oleic acid series probably some members between $C^{20}H^{18}O^4$ and $C^{34}H^{18}O^4$; and besides these,

crotonic acid of the formula $C^8 H^6 O^4$ and angelicic acid, $C^{10} H^8 O^4$. All these acids are contained as glycerides in the fresh oil.

It also appears from the author's experiments, that the crotonic acid is neither the caustic nor the purgative matter. The caustic matter of croton oil is a resinous body, *crotonole*, the formula of which is $C^{18} H^{14} O^4$, or a multiple of it.

The frequently peculiar odour of fresh croton oil, which has the greatest similarity with the decoction of Senega root, is due to a product of decomposition of the crotonole. Another product of its decomposition is the volatile oil of previous observers.

The caustic matter in croton oil, crotonole, has no purgative action; the latter property belongs to another body which was not detected.

With regard to crotonic acid, the author shows particularly that it forms a member of the oleic series lying between angelicic acid and acrylic acid. As angelicic acid, when fused with potash, furnishes acetic and propionic acids, so crotonic acid gives 2 equivs. acetic acid

$$C^8 H^6 O^4 + 2KHO^2 = 2C^4 H^3 KO^4 + 2H.$$

Crotonic acid occurs with angelicic acid, after the saponification of the oil with solution of soda, in the nearly black subjacent fluid. This is distilled with tartaric acid; the distillate is saturated with baryta and evaporated, the baryta-salt is again distilled with dilute tartaric acid, and this is repeated until the distillate passes over free from muriatic acid; lastly, the neutral baryta-salt is prepared, and the dry salt is heated with a solution of phosphoric acid of such strength that it boils at 226°·4 F. The crotonic acid then separates as a limpid liquid, and floats on the surface of the fluid.

The crotonates of potash and soda are deliquescent. The baryta-salt is readily soluble, and forms an amorphous, white mass; it always smells like the free acid.

The above-mentioned soluble salts gave precipitates with many metallic compounds; at the same time the odour of the free acid was almost always perceptible, which may be due to the partial formation of basic salts. With protosalts of iron brownish-yellow precipitates are produced; persalts of copper form pale blue precipitates, which appear nearly white in small quantities. The analysis of a precipitated copper-salt, dried *in vacuo* over sulphuric acid, gave the proportion 1 Cu to 5·7 C. Solutions of lead, mercury, and silver gave white precipitates. A precipitate formed by nitrate of silver and crotonate of baryta was amorphous and white when dried; it became brown slowly when exposed to the sun, more rapidly at 212° F., and was tolerably soluble in hot water.

Crotonate of Silver, $C^8 H^5 Ag O^4$, obtained by boiling the aqueous distillate from the baryta-salt and tartaric acid with oxide of silver, was crystallized, and gave on analysis—

C	24·57	24·40	8 =	48	24·87
H	2·62	2·80	5	5	2·59
Ag	55·90	56·13	1	108	55·95
O	16·91	16·67	4	32	15·59

The active matter of croton oil, to which the author gives the name of

Crotonole, is obtained in the following manner. Croton oil is agitated with a sufficient quantity of an alcoholic solution of soda to form a milky fluid; this is gently heated for some hours, and then, by the addition of water or of solution of chloride of sodium, the milky oil-particles are driven to the surface, where they unite to form a continuous oily stratum. This fatty oil is entirely got rid of by repeated filtration through a moist filter. From the filtrate, water and muriatic acid separate another oil, which is dissolved in cold alcohol, and mixed with fresh hydrated oxide of lead; by this means a flocculent precipitate is formed, which towards the end often coheres to form a slimy mass. When the acid reaction has entirely disappeared, a little soda and a large quantity of water are added, by which the fluid is first rendered milky, but afterwards divides into a clear fluid and a clear oil which sinks to the bottom. To attain this, an addition of large quantities of chloride of calcium to the alcoholic solution was frequently indispensable. The oil thus separated is washed with water for some time upon a moist filter, and then dissolved in æther; the ætherial solution is agitated with water in a cylindrical glass, the clear ætherial solution is drawn off and freed from æther in a capsule *in vacuo*. The crotonole remains as a tenacious mass, resembling thick turpentine. It is colourless, or of a slight wine-yellow colour. The odour is weak and peculiar. In its properties it most closely approaches the alcohols.

When boiled with solution of potash or soda, crotonole is converted into a brown, resinous matter, which has no action upon the skin.

When boiled with water, or still better with dilute sulphuric acid, an oil with a mouldy odour appears to be formed; this passes over in considerable quantity when water acidified with sulphuric acid, in which croton oil is suspended, is distilled; it floats upon the distillate, without being dissolved in the least. It is only the oil which passes at the commencement that is colourless, for it soon goes over nearly black. Without the assistance of aqueous vapours it is not distillable; for in a space exhausted of air to a pressure of 50 millims. nothing could be distilled even at 392° F.; but by this means it became black and entirely lost the mouldy odour; it had also become far more soluble in æther. The croton oil obtained by pressure contained 4 per cent. of crotonole.—Liebig's *Annalen*, cv. p. 1.

ANALYTICAL CHEMISTRY.

On the Analysis of Hæmatite and Magnetic Iron Ores, and the Separation of Oxide of Iron from Alumina. *By* WILLIAM WALLACE, Ph.D., F.C.S., *Glasgow**.

IN the 'Comptes Rendus' for July 1850 (xxxi. 82) M. Ch. Mène published a new volumetric method for the estimation of tin, in

* Communicated by the Author.

which sesquichloride of iron was recommended as the oxidizing agent. For some time prior to the publication of M. Mène's paper, a solution of protochloride of tin had been employed by Dr. Penny in the laboratory of the Andersonian Institution for the determination of peroxide of iron. A dilute solution of the tin-salt was added to the liquid containing peroxide of iron until a drop of the latter no longer communicated a red colour to sulphocyanide of potassium. The strength of the tin solution was afterwards ascertained by an analogous experiment with bichromate of potash. In the application of this method to the analysis of hæmatite and magnetic iron ores, a difficulty, however, existed in obtaining the necessary solution, as these ores are so difficultly soluble in even the strongest hydrochloric acid, that several hours are required to dissolve the quantity necessary for the analysis. This difficulty has been removed by the discovery by Mr. Hutton of the Andersonian Laboratory, that if the tin solution is added gradually as the oxide of iron dissolves, the process may be completed in a few minutes. Mr. Hutton's interesting observation shows that sesquioxide of iron is readily soluble in a strongly acid solution of protochloride of iron, while it is difficultly soluble in a similar solution of the sesquichloride.

Having lately had occasion to practice this valuable process very extensively, I have endeavoured to bring it to the greatest possible perfection, and have applied it to various useful purposes. I intend, in the present paper, to describe some of these applications, in the hope that they will prove serviceable to analytical chemists generally, and particularly to those who are engaged in prosecuting the analysis of minerals in connexion with the smelting of iron.

I have found that the most accurate results are obtained by employing, as the determining agent, either permanganate or bichromate of potash, the latter being the most suitable in consequence of its constant composition. I have tried all the ordinary reducing agents for the reduction of the peroxide of iron to the state of protoxide, and have concluded that protochloride of tin is the only one which is capable of effecting a sufficiently rapid deoxidation. In point of accuracy the process about to be described is not surpassed by any volumetric method of analysis at present in use. By a series of experiments I have satisfied myself, that with careful manipulation the error need not exceed ·2 per cent.

Analysis of Hæmatite and Magnetic Iron Ores.—From 1—2 grms. of the pulverized ore* are introduced into a small flask, together with half an ounce of the strongest hydrochloric acid, and the mixture is heated. A solution of protochloride of tin of spec. grav. 1·6 (called by drysalters "double muriate of tin") is now gradually dropped in until the powder is entirely dissolved, or at least all the oxide of iron is dissolved, and the liquid becomes of a pale yellow colour. This will occupy only about three minutes, if heat is applied during

* Great care is necessary in reducing these minerals to powder, as some of them are so hard that, if pulverized in an ordinary cast-iron mortar, so much of the latter is removed by attrition, that the resulting powder may contain 1 or 2 per cent. of metallic iron.

the process. A mixture of 5 parts of the tin solution with 95 parts of water is now added from a burette until the iron solution becomes quite colourless. It is quite superfluous to apply any test in order to ascertain the exact point at which the reduction is completed; the colour of the liquid is a sufficient guide. Indeed, this colour-test is so delicate, that when the liquid has a slight but still very distinct yellow colour, the addition of a single drop of the dilute tin solution will serve to render the mixture perfectly colourless. The error, therefore, which may arise from the addition of too great a quantity of the reducing agent is, with careful working, limited to one drop of the diluted tin liquor.

The concentrated tin solution is conveniently added from a little piece of apparatus which I have found useful in many processes of analysis. It consists of a cylindrical pipette adapted to contain 10 burette divisions. The upper end of the instrument is connected with a piece of caoutchouc tubing, provided with a screw-clamp, by which the passage of the liquid is regulated with the utmost nicety. A short glass tube attached to the other end of the caoutchouc connecter serves for sucking up the tin liquor. The instrument is fixed to an arm of a retort stand.

The solution containing the reduced oxide of iron is now largely diluted, and the iron determined by either of the well-known processes of Margueritte or Penny. 100 parts of bichromate of potash are equivalent to 88 parts of metallic iron, or 125·7 of sesquioxide.

When magnetic iron ore or roasted clayband or blackband is the subject of analysis, it is necessary to perform two experiments, in order to determine the respective quantities of protoxide and sesquioxide. If the mineral dissolves readily in hydrochloric acid, the protoxide is estimated in the usual manner, and the total amount of iron by the process already described; but if it is difficultly soluble, the two oxides may be estimated by a single experiment, as follows:—A convenient quantity (1—2 grms.) is heated with half an ounce of hydrochloric acid, as already described. A burette is prepared with dilute tin solution (1 part of "double muriate of tin" to 9 parts of water), and this is gradually added until all the sesquioxide of iron is reduced. The number of divisions consumed having been carefully read off, a similar experiment is at once made with 1 grm. of pure recently ignited sesquioxide of iron, the remainder of the liquor in the burette being used for the reduction. A simple calculation gives the amount of peroxide in the ore. The total quantity of iron is estimated by bichromate or permanganate of potash.

Separation of Sesquioxide of Iron from Alumina.—These bases occur together so frequently, that a simple yet accurate method for their separation is a matter of considerable importance. I have obtained highly satisfactory results with the following process, and confidently recommend it for its simplicity, accuracy, and rapidity of execution. The two oxides are thrown down together by ammonia, and the precipitate is collected, dried, and ignited in the usual manner. The weight having been ascertained, the precipitate

is reduced to powder in a small mortar; the powder is ignited to expel traces of moisture which may have been absorbed from the atmosphere, and then weighed*. The sesquioxide of iron contained in the precipitate is now estimated by the process already given for hæmatite iron ores, and a calculation is made for the loss sustained in powdering. The difference between the original weight of the precipitate and that of the oxide of iron indicates the amount of alumina. The experiment is equally successful whatever the proportion of the two bases may be. I have found this process very useful in the estimation of alumina and iron in clayband ironstone and in soils.

In certain cases the above process is applicable to the estimation of phosphoric acid, and may be conveniently substituted for Berthier's method when the substance to be tested already contains a portion of iron.

On the Testing of Milk. *By* Professor C. Brunner.

If milk were simply a compound or even a mixture of water and fat (butter), its specific gravity would doubtless furnish the readiest and most certain indication of its goodness, that is to say, supposing that this might be determined essentially by the amount of butter, it being clear that as the amount of this constituent increases, the specific gravity will decrease in the same proportion. It would be easy by experiments to prepare tables, which, when corrected for temperature, would show the centesimal amount of butter. We should have the same case as with mixtures of water and spirit, such as brandy.

The affair, however, is not so simple, for, as is well known, the aqueous portion of the milk, besides caseine, contains sugar of milk, certain salts, and a small quantity of a still unknown organic substance (the so-called extract of milk). Now, as there can be no doubt that these constituents are subject to certain quantitative variations, and that their quantity has an influence upon the specific gravity in an opposite direction to that of the butter, it is easy to see that the mere observation of the specific gravity of milk cannot lead to any certain conclusions as to the amount of butter contained in it, or as to its comparative value.

This is a similar case to that of wine, in which the variability of the amount of sugar renders the areometer quite useless in determining the proportion of alcohol. Just as with this fluid the separation of the alcohol by distillation furnishes the only means of determining the quantity of this constituent, so, in the case of milk, the preparation of the butter itself could alone lead to the desired result.

This, indeed, has always been perceived, and it is only the endeavour to possess a method of testing which could be easily carried out by any police-officer or purchaser of milk that has produced

* When the proportion of alumina is small, it is unnecessary to pulverize the ignited precipitate.

the various instruments and methods (such as that of Quevenne*), founded partly upon areometry and partly upon a mechanical and usually very imperfect separation, which have gradually been brought into use.

A complete analysis of the milk to be examined is hardly adapted for general use. On the other hand, a process, by which that constituent which may be regarded with some justice as the most essential one, may be determined without too great loss of time, may probably be sufficient in most cases. This constituent in milk is the butter; to determine which the following process may be adopted:—

A carefully weighed quantity, 20 grms. for example, of the milk to be examined, is mixed with half its weight (10 grms.) of thoroughly calcined, coarsely pounded wood charcoal, freed from fine powder by sifting; the mixture is thoroughly dried by a gentle heat (about 158°—176° F.), and then put into a glass tube of about 2 feet in length and half an inch in diameter, somewhat drawn out at one end. To prevent the powder from falling through the lower, narrower opening of the tube, it is lightly stopped with cotton. When thus arranged, the tube is held in a perpendicular position by means of a stand. About 30 grms. of æther are then poured over the contents of the tube; this of course penetrates immediately through the charcoal powder, becomes charged with the dissolved butter, and flows down into a glass placed underneath. In order that the solution may be complete, the æther is poured again once or twice over the charcoal powder, after which 30 grms. of fresh æther are poured in small portions, and any æther that may have remained in the charcoal is displaced by the same quantity of a mixture of 1 part of æther and 3 parts of alcohol. The whole of the fluids are then evaporated by a gentle heat in a small porcelain capsule, and the butter obtained is weighed.

To judge of the accuracy of which this process is capable, several samples of the same milk were repeatedly submitted to experiment. The differences were 1—2 per 1000. It must, however, be remarked that with milk with a large amount of butter, for example, with cream, a large quantity of æther, or if it be preferred, a smaller quantity of the fluid to be examined must be taken.

With several samples the following values were obtained:—

Milk.

I.	From	20 grms.	0·612	butter =	3·06	per cent.
	„	20 „	0·632	„	3·16	„
II.	„	20 „	0·701	„	3·505	„
	„	20 „	0·712	„	3·56	„
	„	20 „	0·705	„	3·502	„

Cream.

From	20 grms.	2·204	butter =	11·02	per cent.
„	20 „	2·126	„	10·63	„

* Instruction pour l'usage de lactodensimétrie, suivie d'une notice sur le lait. Paris, 1842.

Many may perhaps find this mode of testing too tedious. It must, indeed, be admitted that it is not adapted for being carried out directly at every town gate, so as to furnish a judgement immediately. On the other hand, it would be very easy to hit upon an arrangement, by which the samples taken on one day might be judged on the following day. At any rate, in particular disputed cases, the method may furnish a tolerably certain result.

The only thing which might perhaps be urged against this process, would be the possibility of deception by the addition of fat to a milk containing but little butter. The author does not know whether such an adulteration has ever been practised, but it would not be easily effected, and would soon betray itself in various ways.

That the same process may be employed in the determination of other emulsion-like fluids can hardly be doubted, but at the same time it appeared advisable to try some experiments on this subject. For this purpose carefully weighed quantities (1—2 grms.) of olive oil were stirred up with gum-arabic and water in the usual way to form an emulsion, this was dried with charcoal powder and afterwards extracted with æther as above described; by this means very nearly the quantity of oil employed was recovered.

The amount of fat in chocolate may also be determined in the same way. A weighed quantity of chocolate is allowed to melt in water; the fluid is dried with charcoal, and the fat extracted with æther in the displacement apparatus. The butter obtained is perfectly pure and of a dazzling white colour.—*Berner Mittheilungen*, December 1857.

On the Behaviour of Perchloride of Iron to Hydriodic Acid. *By* Carl Mohr.

If to a moderately concentrated solution of perchloride of iron a large quantity of iodide of potassium in substance be added, and the separated iodine be removed by a few crystals of sulphite of soda, a clear fluid is obtained, which, on the addition of cyanide of potassium and caustic potash, furnishes a clear solution of ferridcyanide of potassium. If the experiment be repeated with a dilute solution of perchloride of iron, flakes of separated peroxide of iron are always observed after the addition of cyanide of potassium. The author proves by experiments, in which he employed the solution of perchloride of iron in a more or less dilute state, that the quantities decomposed become smaller as the solutions are more diluted, so that with concentrated solutions of perchloride of iron the quantity of iodine separated corresponds with the amount of perchloride of iron, whilst with dilute solutions only a partial separation of iodine takes place. The author calls attention to the fact that Duflos's method of determining iron, as well as the modified method of Streng, which are founded upon this reaction, require to be very cautiously carried out, and also adds that the determinations are rendered quite uncertain by the circumstance that when the iodine separated has been measured by the hyposulphite of soda, the

reaction of iodine again makes its appearance. The subsequent blue coloration occurs slowly in concentrated solutions, and rapidly and permanently in dilute solutions.

The reason of this is that as the dilution increases, the quantity of iodine separated diminishes, so that perchloride of iron remains undecomposed. Consequently that fluid which still contains the largest quantity of perchloride of iron will effect a new separation of iodine with the greatest rapidity, and this case occurs when dilute solutions are employed. The degree of dilution at which no separation of iodine occurs, or at which perchloride of iron and hydriodic acid may exist side by side without mutual action, was determined by experiment. 5 cub. cent. of a solution of perchloride of iron, containing 0·0415 grm. $Fe^2 Cl^3$, were mixed with 5 cub. cent. of solution of iodide of potassium (0·5 grm. of the salt), and gradually diluted more and more, when the intensity of the blue colour was estimated by the addition of solution of starch.

1 $Fe^2 Cl^3$	: 5060	volumes,	intense blue colour.
1 „	: 7470	„	pale blue colour.
1 „	: 9879	„	no blue colour at first; slight blue colour after the lapse of a few moments.
1 „	: 12289	„	no blue colour; very faint after long contact.

If the process be modified by adding the solution of potash first, and then diluting with water, the solution may be greatly diluted without diminishing the blue coloration of the iodide of starch.

In opposition to the statement that iodine has no action upon solutions of protoxide of iron, the author remarks that this is altered when the solutions are diluted. When a solution of protosulphate of iron, which when concentrated takes up no iodine, is moderately diluted before or after the addition of a solution of iodine, considerable quantities of iodine will be consumed before the iodide of starch makes its appearance. Iodine is therefore partially taken up by the neutral solution of a protosalt of iron until the formation of periodide takes place.—Liebig's *Annalen*, cv. p. 53.

A Sensitive Reagent for Grape-sugar. *By* J. Löwenthal.

60 grms. of tartaric acid and 120 grms. of crystallized carbonate of soda are dissolved in 250 grms. of water. 120 grms. of the same carbonate of soda are also dissolved in another 250 grms. of water, and the two solutions when cold are poured together. Lastly, 5—6 grms. of crystallized perchloride of iron are added; the whole is boiled for a few minutes, and filtered.

This solution, when boiled, remains clear pale yellow. But if it be boiled with a very small quantity of grape-sugar, it becomes darker, and if the amount of grape-sugar be not too small, it grows turbid, and deposits a voluminous precipitate which contains protoxide of iron.—*Journal für Prakt. Chemie*, lxxiii. p. 71.

THE CHEMICAL GAZETTE.

No. CCCLXXIX.—August 2, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Occurrence of Urea, Taurine, and Scyllite in the Organs of the Plagiostomous Fishes. *By* G. STÄDELER *and* F. T. FRERICHS.

IN continuing their investigations upon the occurrence of leucine and tyrosine in the organs of man and animals, which now extend over all classes of animals with the exception of the Polypes and Infusoria, the opinion formerly expressed by the authors, that these bodies must be regarded as important products of the changes undergone by matters in the organism, has been completely confirmed. It is only in a few classes of animals, as in the *Entozoa*, the *Acalephæ*, and a few others, that the authors have not hitherto been able to detect these bodies, whilst others, especially the Crustacea, Arachnida, and Insects, are distinguished by their abounding in leucine and partly also in tyrosine. Sometimes uric acid occurs therewith in very considerable quantity, for example, in all Insects; sometimes this body is entirely wanting, as the authors found to be the case in the Crustacea and Arachnida. They also repeatedly observed the presence of considerable quantities of sugar in those cases in which leucine was wanting, especially in the Entozoa and some bivalve Mollusca, and also in hydropic fluids; and this appears to be the more worthy of notice, as they tested numerous diseased livers, which were rich in leucine, and found no sugar in them. That these two bodies mutually exclude each other, can, however, by no means be asserted, for in some cases the reaction of sugar was obtained together with leucine; nevertheless the uncertainty of the reaction must still be taken into consideration, as it has been found that leucine also reduces the alkaline solution of copper.

In the autumn of 1856 the authors received, with various other marine animals, some Rays (*Raja Batis* and *R. clavata*) and a large Dog-fish (*Scyllium canicula*) of about 7 feet in length, from the coast of Norderney. From the Dog-fish the authors collected abou ¾ths of a pound of blood and 1 pound of the liver, which wa 29 pounds in weight, and also the spleen, pancreas, kidne

gills, heart, and ovary; from the Rays they took the liver, spleen, pancreas, kidneys, testes, glands of the oviducts and gills. These were investigated in the fresh state.

The organs were triturated with coarsely powdered glass, stirred up with 1½ to 2 volumes of alcohol, and pressed; the residue was again treated with a small quantity of alcohol. The blood was treated in a similar way, and the whole of the residues from the pressure were removed.

The extracts thus obtained were filtered and the alcohol evaporated; the residues were taken up by water, the solution filtered from the oil or other fatty and partly also gelatinous matters, and again evaporated to a thick syrup. By treating this with hot absolute alcohol, letting it stand for 24 hours, and filtering it, it was again divided into two parts, a slightly coloured soluble portion, and a brown insoluble residue.

The alcoholic extract was first of all freed from alcohol by evaporation, and when fatty matters had again separated, was taken up by water, and precipitated by basic acetate of lead; the filtrate was freed from lead by sulphuretted hydrogen, and evaporated to a syrup. This syrup contains in some cases a little leucine, once (from the spleen of the Dog-fish) a trace of tyrosine, but always urea in considerable quantity.

The residue was sometimes perfectly amorphous, but sometimes it contained crystals. In the latter case it was dissolved in water and left to evaporate spontaneously, and as soon as the crystallization was completed, placed upon moistened blotting-paper to absorb the mother-liquor. The crystals usually remained perfectly colourless, and could be separated mechanically from some intermixed chloride of sodium; they consisted of taurine or of a peculiar body similar to inosite, which the authors call scyllite, and sometimes of a mixture of both. The separation of the two bodies was easily effected by means of basic acetate of lead, which throws down the scyllite in the form of a lead-compound, whilst the taurine remains in solution. In one case (the spleen of the Dog-fish) a small quantity of tyrosine was also obtained; it occurred together with taurine, and could be separated therefrom by means of its difficult solubility. (The authors also found taurine in the adductor muscle of the oyster.)

Leucine and tyrosine appeared to be entirely wanting in the organs of the Rays; it was only in the testes that some forms were observed which might be leucine. In the blood and several organs of the Dog-fish also, neither of these bodies was found; leucine was undoubtedly recognizable only in the spleen, the pancreas, the gills, and the ovary. In the spleen there was also a small quantity of tyrosine.

Creatine could be detected with certainty in none of the organs; not even in the heart of the Dog-fish. When it occurs in investigations, it is found in the residue in which scyllite and taurine are met with.

All the organs of the Rays and Dog-fish, with the exception of

the spleen, pancreas, gills and ovary of the latter, were examined for urea. Everywhere enormous quantities of urea were present, so that the syrup, when mixed with an equal volume of nitric acid, solidified into a solid paste. In the liver of the Dog-fish, notwithstanding its great abundance of fat, it may be calculated that there are at least 2 ounces of urea; and all the other organs, and even the blood, were comparatively far richer in that body.

Uric acid was only sought for in one instance; it could be detected in the liver of the Dog-fish.

Taurine was found in the greatest abundance in the blood of the Dog-fish; in smaller quantities in the liver, spleen, and kidneys of the Rays.

Scyllite was found most abundantly in the kidneys of the Ray and Dog-fish; it also occurred in the liver and spleen of the former, and in the liver and gills of the latter.

Scyllite is a body free from nitrogen and sulphur, which has much resemblance to inosite, but dissolves with far more difficulty in water, and shoots very readily into hard, glassy crystals, which are sometimes of considerable size. The crystals are clinorhombic prisms. They are sometimes tabular, and when rapidly separated exactly similar to those of inosite. But they contain no water of crystallization, and consequently do not effloresce either in the air, or when gently heated; and when treated with nitric acid, ammonia and chloride of calcium, they give no reaction of inosite. Their taste is slightly sweetish. When heated upon platinum foil scyllite burns with a clear flame, leaving a coal which may be easily burnt. In a glass tube it fuses with some difficulty, swelling up, and becoming blackened; with a stronger heat carbonization occurs with evolution of acid vapours, smelling like burnt sugar.

The aqueous solution has a perfectly neutral reaction, and is not precipitated by acetate of lead; it furnishes a pasty precipitate after the lapse of a few moments with basic acetate of lead. This reaction agrees precisely with that of inosite. If the lead-compound be suspended in water and decomposed by sulphuretted hydrogen, scyllite crystallizes again from the filtrate when evaporated. It is insoluble in absolute alcohol, and is separated from the aqueous solution on the addition of alcohol, either as a heavy crystalline powder, or, if the alcohol be added very slowly, in beautifully developed, brilliantly glassy, individual crystals.

Nitric acid of spec. grav. 1·3 does not dissolve scyllite in the cold; when boiled it is dissolved slowly, without any evolution of gas. The solution contains unaltered scyllite, which is separated again in its original form and free from nitrogen on the addition of alcohol. Concentrated sulphuric acid, both when cold and gently heated, has no action upon scyllite; but when more strongly heated, decomposition takes place with evolution of sulphurous acid, the solution becoming first yellow, then red, and finally reddish brown. Scyllite may be boiled with concentrated solution of soda without acquiring any colour; it does not reduce an alkaline solution of copper.

Scyllite is evidently nearly allied to inosite, not only in several of

its reactions, but even as regards its occurrence; for whilst the latter occurs in the greatest quantity in the kidneys of healthy men and the higher animals (oxen), scyllite is met with in the greatest abundance in the kidneys of the above-mentioned cartilaginous fishes. Perhaps both bodies have the same composition; for the present, the material was unfortunately insufficient to enable an elementary analysis to be made, as it was especially important to ascertain the properties of scyllite, and to determine the identity of the crystals occurring in the various organs.

In the organs of the bony fishes the authors have found neither taurine, scyllite, nor urea. They investigated the organs of the Haddock and Pike. As the latter lives entirely upon fishes, it appeared from this at the same time that the food has no essential influence upon the formation of these bodies, which was still further confirmed by the fact that they were not to be found in the organs and blood of the Seal. In the blood there was indeed a trace of urea, but not more than is found in the blood of all the higher animals.

Thus the occurrence of these bodies appeared to be peculiar to that section of the fishes which are usually known as Cartilaginous fishes. According to the older classifications, this group includes the Sturgeons, the *Selachii* (Sharks and Rays, and some others), and the Lampreys. Of the latter, the authors have examined the River Lamprey (*Petromyzon fluviatilis*) for urea with a negative result; nor did they meet with it in the alcohol, in which the intestines of the common Sturgeon (*Acipenser Sturio*) had been preserved for years, so that the occurrence of urea appears to be limited to the *Selachii*, or to the group of fishes which have lately been characterized as *Plagiostomi*, including the Rays and the Sharks.

In the muscles and kidneys of *Spinax acanthias* the authors also found an enormous quantity of urea; in the muscles together with much creatine, and in the kidneys with some taurine and scyllite, whilst leucine and tyrosine were not present.

All the organs of the *Plagiostomi* investigated by the authors, appeared to be in a manner soaked in a tolerably concentrated solution of urea.—*Journal für Prakt. Chemie*, lxxiii. p. 46.

On the Identity of Nitrosalicylic Acid with Anilotic Acid. *By* A. Strecker.

Anilotic acid is the name given by Piria to an acid which he obtained by the treatment of salicine with nitric acid of spec. grav. 1·19; he noticed that it had much resemblance to nitrosalicylic acid. H. Major subsequently occupied himself with this acid in Strecker's laboratory. He convinced himself that anilotic acid is identical with nitrosalicylic acid. Strecker now proves that this assertion is correct.

Anilotic Acid has the same formula as nitrosalicylic acid. 100 parts of water dissolve 0·066 of anilotic acid, and 0·065 of nitro-

salicylic acid. Both acids crystallize from their hot saturated solutions in an anhydrous state. From the ætherial solution both acids may crystallize in an anhydrous and, under certain circumstances, in a hydrated state. The amount of water in nitrosalicylic acid was determined by Marchand at 11·6 and 10·7 per cent.; he also found that the crystals lose this water even by exposure to the air. The author likewise found this to be the case. He determined the amount of water in anilotic and nitrosalicylic acids crystallized from æther, and found—

In anilotic acid, crystallized in needles from æther, 12·2 of water.

In nitrosalicylic acid, prepared from salicylic acid and crystallized in needles from æther, 13·2, 12·9, 12·7, and 12·9 of water.

Both therefore contain 3 equivs. of water of crystallization (calculated 12·8 per cent.).

The baryta-salt of anilotic acid, obtained by boiling the solution of the acid with carbonate of baryta, gave 30·3 per cent. of baryta and 11·7 per cent. of water. The basic salt obtained by precipitation with baryta-water lost scarcely any water at 212° F. At 284° —302° F. it lost 9·6 and 9·4 per cent. of water. The salt dried at 302° F. gave 45·5 per cent. of baryta.

The first salt is therefore $C^{14} H^4 NO^9, BaO$,
the second, $C^{14} H^4 NO^9, BaO + BaO, HO + 4HO$,
and after drying, $C^{14} H^4 NO^9, BaO + BaO\,HO$.

The only difference which remained after the comparison of Piria's statements with the author's observations upon this acid, was, that the potash and ammonia salts of anilotic acid with 1 equiv. base, are white, and only become yellow by excess of base. The author never obtained these salts quite colourless, but pale straw-yellow. As, however, a little picric acid may easily be mixed with nitrosalicylic acid, the author thinks it cannot be doubted that Piria's anilotic acid was nothing but very pure nitrosalicylic acid.—Liebig's *Annalen*, cv. p. 299.

On some of the Products of the Destructive Distillation of Boyhead Coal.—Part II. *By* C. Greville Williams, *Lecturer on Chemistry in the Normal College, Swansea.*

The first part of this paper contained the results of the examination of those hydrocarbons found in the distillate from the Torbanehill mineral which were remarkable for their resistance to the action of monohydrated nitric and sulphuric acids. It was shown that, when in a state of purity, they possessed the composition, boiling-point, and density in the fluid and gaseous states, of the radicals of the ethylic class of alcohols. The present communication enters on the study of a group of substances as distinguished by the mobility, as the former are by the fixity of their hydrogen atoms. The examination of them has involved more labour than was experienced with their companion hydrocarbons; and the quantities obtained being necessarily small, even when working on a considerable scale,

it has been impossible, at present, to do more than determine their constitution. The study of their combinations and decompositions is therefore necessarily deferred.

Up to the present time we have been unacquainted with methods for the proximate analysis of complex mixtures such as that under study. It was necessary, therefore, to devise some plan for the purpose. The presence of benzole and its homologues was almost a matter of certainty, as they appear to be formed in all processes where coaly or bituminous matters are subjected to destructive distillation. In order to separate the hydrocarbons, the following method was adopted. Four ounces of bromine being placed in a large and well-stoppered flask, about 8 vols. of water were added. The naphtha boiling in the fourteenth rectification between 71° and 77° Centigrade, was then added in very small portions, the whole being violently agitated after each addition. As the bromine, from its superior density, lay at the bottom of the water and the naphtha at the top, it will be seen that combination could not take place until the flask was shaken, at which time they united with a sharp hissing sound and a rise of temperature. The entire quantity of naphtha was absorbed by the bromine, forming a dense oil, becoming paler and at last colourless as the hydrocarbon increased in quantity. To ensure a definite product more bromine was used, so as to obtain a red oil, the excess being afterwards removed by agitation with mercury. During the process some substance is generated, acting powerfully on the eyes and causing a flow of tears; it is always present in the brominated oil, even when every trace of free bromine is removed. If the brominated oil be kept for some time in contact with water, it will be found that a third layer will make its appearance beneath the oil; this will be described hereafter.

On the crude bromine compound being separated and distilled, all the benzole and radicals will distil away, leaving the brominated oil, the boiling-point of which is much higher. We are not acquainted with any process for separating benzole from the radicals in such a manner as to yield the former pure, but by treatment with fuming nitric acid, in the manner described in Part I., the benzole is transformed into the nitrocompound, from which the propyle may be obtained by distillation on the water-bath.

It was necessary to ascertain whether the nitrocompound obtained by treating with nitric acid the fluid distilling away from the brominated oil, contained any substance (save nitrobenzole) capable of forming alkaloids by reduction. On treatment by Béchamp's process, it yielded a considerable quantity of base having all the characters of aniline, and distilling at 182°.

To confirm this result a portion was dissolved in hydrochloric acid, and to the solution was added about a third of the quantity of bichloride of platinum necessary to precipitate the whole of the base in the state of platinum salt. The precipitate being filtered off, a fresh quantity of the bichloride was added, and so on until three precipitates were obtained. They were washed with a mixture of alcohol and æther previous to drying.

Analysis gave—

	Experiment.				Calculation.	
	1st precip.	2nd precip.	3rd precip.			
Carbon	24·5	24·5	..	C^{12}	72·0	24·0
Hydrogen..	2·9	2·9	..	H^{8}	8·0	2·7
Nitrogen ..	..	..	..	N	14·0	4·7
Chlorine ..	..	..	..	Cl^{3}	106·5	35·6
Platinum ..	32·6	32·6	32·7	Pt	99·0	33·0

It is evident, therefore, that the aniline procured in this manner is almost pure, the only admixture being a small portion of toluidine; and it may with safety be concluded that benzole is the only hydrocarbon (distilling away from the brominized oil) which forms a nitrocompound capable of reduction by protacetate of iron.

If the bromine compound obtained from the naphtha boiling between 71° and 77° be distilled, a thermometer being in the tubulature of the retort, no constant boiling-point will be obtained until a temperature of 123° is reached. This arises from the tenacity with which the oil retains benzole and the radicals. It was only after much labour and numerous analyses that this source of difficulty was discovered, and precautions taken to prevent its interfering with the isolation of the hydrocarbons to be presently described. If the heat be very gradually applied to the retort, ebullition will commence at about 80°, the mercury rapidly rising until 123° is reached, after which the rise becomes very slow. When the propyle and benzole have distilled away, and the point of ebullition of the fluid is elevated to 150° or upwards, rapid evolution of hydrobromic acid takes place, accompanied by a vapour acting powerfully on the eyes. The distillate at this point acquires a fine blue colour. It being plain from these phænomena that the hyperhalyde produced by the action of bromine could not be prepared in a state fit for analysis, the residue in the retort was mixed with a strong alcoholic solution of potash, in order to obtain a halyde capable of being distilled without decomposition. On mixing the two fluids there was a great rise of temperature, and a large quantity of bromide of potassium crystallized out. Sometimes the bromine compound and the alcoholic potash were cohobated together, at others the halyde was prepared by mere digestion of the ingredients and subsequent precipitation of the oil by water; even cohobation over solid hydrate of potash produced the same result. The brominated oil thus prepared was colourless, very dense, and had a powerful odour, somewhat resembling iodide of amyle. Although the hyperhalyde was prepared from a fraction of almost constant boiling-point, and purified carefully by distillation on the oil-bath, all coming over below 130° being rejected, yet the halyde produced from it was not homogeneous, its boiling-point varying from 80° to 150°.

MM. Berthelot and De Luca have shown in their memoir on iodized propylene the great difficulty of obtaining pure products of this class, owing to the simultaneous formation of other substances, both fixed and volatile; and it is evident that if such a difficulty is found with that substance, it must exist to a much greater extent

with a homologue having so comparatively high an atomic weight as that yielding the compound under consideration. In order to lessen the sources of error, the bromine compound was fractionated previous to analysis, but, despite every precaution, numerous and perfectly concordant analyses showed the impossibility of obtaining it free from oxygen. This arose from the mode of preparation. The formula of the brominated oil was, originally, $C^{12} H^{11} Br$, but oxidation had proceeded so far as to make the composition almost agree with the expression $C^{12} H^{11} BrO$. The cause of the oxidation of the monobrominated caproylene or hexylene will become apparent from the following experiments.

It has been said that when the hydrocarbons were treated with bromine in presence of water, the fluid separated after a time into three layers, the upper being water containing a small quantity of hydrobromic acid, the middle the brominated oil, and a lower stratum. The latter, on separation by a tap-funnel, proved to be highly acid and perfectly soluble in water. It distilled, with very little evolution of acid fumes, at 127°. A piece of paper moistened with it and held near the fire, became jet-black at the spot touched. Excess of precipitated carbonate of lime was added, and, as soon as effervescence had ceased, the whole was boiled for a few minutes and filtered. The solution evaporated to dryness yielded a white and highly deliquescent mass, a qualitative analysis of which indicated the presence of bromine and calcium. A portion was heated to redness, rapidly cooled in a platinum crucible with a well-fitting lid, and the per-centage of calcium estimated.

	Experiment.	Calculation.	
Bromine	79·85	Br	80
Calcium	20·15	Ca	20

The ignited salt, on being moistened with warm water, became extremely hot, and hissed like hot metal when quenched.

The preceding salt being deliquescent, and consequently not convenient for analysis, I digested a fresh portion of the acid upon carbonate of baryta, the latter being in excess; the solution was boiled, filtered and evaporated to dryness on the water-bath. After two hours' desiccation at 100°, it gave on a determination of the barium 43·67 per cent., corresponding to the formula Ba Br, HO; requiring 43·53. By ignition the per-centage of barium was raised to 46·8. Ba Br requires 46·16. During ignition the salt became grey, but regained its original appearance when moistened with water.

A determination of the per-centage of dry hydrobromic acid in the fluid afforded 37·2 per cent.

The specific gravity of the fluid obtained in this singular manner was 1·320 at 18°. The small quantity of fumes evolved during the distillation points to the existence of a definite hydrate; H Br + 15HO would contain 37·5 of hydrobromic acid, a number not far from that found by experiment. The reason for examining thus minutely the lower layer of liquid, was to trace the nature of the reaction resulting in the production of the oxidized fluid. It is plain that water was decomposed by the excess of bromine;

the oxidation therefore resembled that produced by the halogens generally.

The examination of the bromine compounds was not pursued further, because their products of decomposition appeared more interesting.

The results detailed render it evident that the only method of studying satisfactorily the $C^n H^n$ group as it existed in the oily fluid would be by means of its derivatives. It is well known that bodies of this class must, after the action of alcoholic potash, be regarded as bearing the same relation to the negative that the hydriodic æthers do to the positive radicals. Like them, the halogen compounds, when decomposed by metals, yield hydrocarbons, having, for 4 vols. of vapour, double the number of atoms of carbon and hydrogen existing in the iodides, bromides, &c., and these hydrocarbons or radicals, as they are still called, have consequently a higher boiling-point than if the number of carbon and hydrogen atoms remained the same. Thus propylene, $C^6 H^6$, is a gas, while allyle, the negative radical, $C^{12} H^{10}$, is a fluid boiling at 59°. It was therefore probable that the hydrocarbon, $C^{12} H^{12}$, would, by treatment of the bromine compound with sodium, yield a derivative boiling at about 116°.

For the purpose of acting on the bromine compound with sodium, a small glass retort was used, into the tubulature of which a large pipette was fastened by means of a cork. The neck of the retort was closed. The pipette being removed and the bromine compound introduced, some freshly-cut fragments of sodium were added. The pipette being returned to its place, the whole was allowed to remain until the action of the sodium, at first energetic, became sluggish in consequence of a coating of bromide covering the metal. Gentle heat was then applied, upon which the fluid entered into ebullition, but the vapours condensing in the pipette constantly returned to the retort. During the reaction the sodium acquired a superb blue colour, reminding us of the phænomena observed by M. Bouis when acting on chloride of capryle with the same metal. The addition of the sodium was continued until no more action occurred, upon which the pipette was removed, and the fluid distilled over. To ensure absence of bromine, it was once more rectified over sodium, but the metal remained perfectly brilliant until the end of the operation.

The fluid thus procured was not the only product, for the bromide of potassium in the retort was mixed with greasy and carbonaceous matters. The hydrocarbon submitted to a fractional distillation came over at 71°, instead of 116°, as would have been the case if the bromine had reacted with sodium in an analogous manner to iodized propylene. The following are the analyses of this fluid:—

	Experiment.		Mean.	Theory $C^n H^n$.
Carbon	85·4	85·7	85·6	85·7
Hydrogen ..	14·3	14·2	14·3	14·3

The bromine compound is therefore decomposed by sodium in a manner totally different to iodide of allyle. To find the value of n, I determined the density of the vapour of the fluid. The operation was performed in an apparatus permitting the experiment to be made at any desired pressure. It was originally intended to ascertain the density at several pressures; the experiment was consequently commenced with an extra column of 205·5 millimetres of mercury, the atmospheric pressure being 759·2. The elastic force of the vapour was therefore equal to a column of mercury 964·7 millimetres in height. On consideration, the idea of making more than one experiment with the vapour of this hydrocarbon was abandoned until its formation had been repeated several times.

Corrections made.

Weight of substance	·4240 grm.
Volume of vapour	116·5 cub. cent.
Atmospheric pressure	759·2 mm.
Extra pressure	205·5 mm.
Temperature of vapour	98°·0
Density.....	3·02

The formula $C^{12} H^{12}$ requires—

12 volumes of carbon vapour	=0·8290 × 12	=	9·9480
24 volumes of hydrogen	0·0692	24	1·6608
			11·6088

$$\frac{11·6088}{4} = 2·9022$$

The excess is partly due to the extra pressure*, but chiefly to the presence of a little $C^{14} H^{14}$.

The fluid procured in this manner is therefore caproylene or hexylene. Its formation by the process detailed is interesting, because it is an instance of the regeneration of a hydrocarbon by means of a complex decomposition similar to that found by MM.

* I have been occupied at intervals during the last two years in ascertaining the amount of influence exercised by pressure on vapour volume, and also in endeavouring to improve the processes generally used for determining the densities of vapours. I hope before long to communicate these results to the Society. In the meantime some values obtained with propyle are annexed, to give an idea of the extent to which the density is increased by pressure.

Vapour-density of Propyle at various pressures.

Theory 2·976 = 4 volumes.

Temperature.	Pressure.	Density.
100°·0	772·1	2·963
97·0	870·6	3·005
97·0	943·8	3·022
98·7	1013·0	3·032

Berthelot and De Luca to occur with propylene. The hexylene is not therefore a mere product of decomposition in the ordinary sense of the term, but is identical in kind with the fluid in the naphtha which yielded the bromine compound. This is proved by the identity of boiling-point. The naphtha distilled between 71° and 77°, and the hexylene produced from it boiled at 71°.

Hexylene was discovered by Fremy * among the products of the distillation of hydroleic and metoleic acids.

Bouis found that chloride of capryle treated with sodium in the cold yielded capryle, but that if the reaction took place with heat, caprylene resulted. It appearing probable from this that the products of the action of sodium on the bromine compounds would vary with the temperature, I repeated my experiments with the necessary precautions.

With the view of obtaining the next homologue of hexylene, the fraction boiling between 82° and 88° was selected. About twelve ounces of bromine were saturated with naphtha in the same manner as before, but, during the treatment of the brominated oil with sodium (after the action of alcoholic potash), all rise of temperature was carefully avoided, the apparatus being constantly covered with cold water. The decomposition is of course more gradual than when heat is applied, but it is quite as perfect.

On redistilling the hydrocarbon, fractions were obtained from 82° to 104°. They were analysed with the following results:—

	I.	II.	III.	IV.	Mean.	Theory $C^n H^n$.
Carbon ..	85·7	86·0	85·5	85·7	85·7	85·7
Hydrogen	14·3	14·4	14·2	14·0	14·2	14·3

The first of these analyses was made on a fluid boiling at 85°, the second and third at 90°, and the fourth at 99°. In order to find the value of *n*, the vapour-density of each of these fractions was determined by Gay-Lussac's method.

Boiling-point.	Weight of liquid.	Volume of vapour.	Difference of level.	Barometer.	Temperature of vapour.	Pressing column of oil in mm. of mercury.	Density.
85°	0·0977	35·75	87·3	755·1	100°	21·7	3·19
90	0·1292	47·50	36·0	732·5	121	20·3	3·22
99	0·1117	43·25	55·0	742·0	146	21·0	3·32

The fraction boiling at 99° has therefore the composition and condensation of œnanthylene or heptylene, the olefiant gas of the œnanthylic alcoholic alcohol, which requires the following numbers:—

14 volumes of carbon vapour..	=0·8290 × 14	=	11·6060
28 volumes of hydrogen.....	0·0692 28		1·9376
			13·5436

$$\frac{13{\cdot}5436}{4} = 3{\cdot}3859$$

* Ann. de Chim. et de Phys. lxv. 139.

The specific gravity of heptylene, in the fluid state, was 0·7184 at 17°.

From these results it is evident that the products of the action of sodium do not vary with the temperature. They also fully confirm the statement, made in another part of this paper, to the effect that the hydrocarbons produced by the processes detailed are identical with those existing in the Boghead naphtha. It will be remembered that the naphtha, from which the bromine compound yielding the heptylene was obtained, boiled between 82° and 88°, and the hydrocarbon produced by the action of sodium on the bromine compound came over between 85° and 99°.

The decomposition which the bromine compound undergoes is by no means simple, large quantities of difficultly combustible charcoal separating, with production of small but distinct traces of fatty acids.

Little is known with regard to the true boiling-points of the $C^n H^n$ series. Those which have been most examined, and consequently appear best adapted for standards with which to compare the boiling-points of the other homologues, do not agree with each other. The boiling-point of amylene, according to Frankland, is 35°; that of octylene was determined by Cahours to be 108°, while Bouis found it 125°. For convenience of reference the following Table is appended, showing some of the physical properties of the best-known members of the $C^n H^n$ family.

Table of the Physical Properties of some of the $C^n H^n$ *series.*

	Observer.	Formula.	Boiling-point.	Density.	Density of vapour.	
					Experiment.	Theory.
Amylene.....	Frankland.	$C^{10} H^{10}$	35	.....	2·386	2·422
Hexylene ...	Fremy*.	$C^{12} H^{12}$	55	.....	2·875	2·904
Hexylene ...	C. G. Williams.	$C^{12} H^{12}$	71	.....	3·020	2·904
Heptylene ...	C. G. Williams.	$C^{14} H^{14}$	99	0·718 at 17°	3·320	3·386
Octylene.....	Bouis†.	$C^{16} H^{16}$	125	0·723 at 17°	3·900	3·875
Octylene.....	Cahours‡.	$C^{16} H^{16}$	108	0·708	3·920	3·875
Nonylene ...	Fremy*.	$C^{18} H^{18}$	110	.....	4·488	4·359

It results from the experiments detailed in the first and second parts of this investigation, that Boghead naphtha consists of a mixture of hydrocarbons belonging to three series, namely,—the radicals of the alcohols; homologues of benzole and homologues of olefiant gas.

Appendix.—Since the reading of the above, I have seen some experiments recently published by Limpricht on the action of perchloride of phosphorus on œnanthole§. He finds the product to be chloride of œnanthylene, $C^{14} H^{14} Cl^2$. By treatment with sodium

* By distillation of hydroleic and metoleic acids.
† By action of sulphuric acid on octylic alcohol.
‡ By distilling pelargonic acid with potash-lime.
§ Chemical Gazette, March 15, 1858.

he obtains œnanthylene (heptylene), boiling at 95°. By first treating the chloride with alcoholic potash to obtain $C^{14} H^{13} Cl$, and then with sodium, he expected, as I did, to obtain $C^{14} H^{13}$, or rather (for 4 volumes of vapour) $C^{28} H^{26}$. The resulting fluid, however, boiled at 95°, and had all the properties of heptylene. One not very satisfactory analysis agreed better with $C^{14} H^{13}$ than $C^{14} H^{14}$, but he admits that the properties of the hydrocarbon agreed so exactly with œnanthylene, that he could not insist on the accuracy of $C^{14} H^{13}$ as the true formula. My experiments, by proving the regeneration of œnanthylene by the action of sodium on $C^{14} H^{13} Br$, show the true nature of M. Limpricht's result. M. Limpricht states $C^{14} H^{13} Cl$ to be without action on sodium at ordinary temperatures; this difference between the chlorine and bromine compounds is curious and worthy of examination.—*Philosophical Trans.* 1857.

On the Glycogenous Matter of the Liver. By Dr. Kekulé.

The glycogene was prepared in exactly the same way as by Bernard. The fear expressed by Lehmann in his admirable summary of the memoirs published on the formation of sugar in the liver, that the boiling of the crude glycogene with solution of potash would scarcely suffice for the complete removal of albuminous substances, proved to be unfounded; half an hour's boiling with only moderately concentrated solution of potash frees the glycogene so completely from nitrogenous substances, that no nitrogen can be detected in it even with potassium. On the other hand, the glycogene prepared in accordance with Bernard's directions, obstinately retains a small quantity of ash (consisting essentially of lime-salts), whilst that prepared by Lehmann's method is almost free from ash. By repeated solution in acids (strong acetic acid, or cold dilute nitric acid) and precipitation with alcohol, the amount of ash may be greatly diminished.

With regard to the properties of glycogene, the author generally confirms the statements of Bernard, Hensen, and E. Pelouze. Glycogene is white, and perfectly amorphous; its aqueous solution is opalescent, even when the substance is perfectly pure. It is coloured violet or usually reddish brown by iodine (like ferrocyanide of copper). The opalescent solution, when boiled with dilute sulphuric acid, rapidly becomes clear, but then shows no sugar reaction; by continued boiling with acid, sugar is readily obtained.

The analysis of glycogene dried at 212° F. gave the following results:—0·2262 grm. gave 0·3690 carbonic acid, and 0·1322 water, leading to the formula $C^{12} H^{10} O^{10}$:—

		Theory.	Experiment.
C^{12}	=72	44·44	44·49
H^{10}	10	6·17	6·49
O^{10}	80	49·39	

The quantity of glycogene obtained in two cases from the liver of rabbits was weighed in the air-dried state.

Weight of the animal.	Weight of the liver.	Glycogene obtained.
1300 grms.	44 grms.	0·8 grm.
1315 „	53 „	1·2 „

The average of the two experiments gives the amount of glycogene as 2 per cent. upon that of the liver.—*Verhandl. des naturhist.-medic. Vereins zu Heidelberg*, January 17, 1858.

On a crystallized Compound of Chromium and Aluminium. *By* F. Wöhler.

This compound was obtained accidentally in experiments made with the object of obtaining chromium in a crystallized form from its perchloride, by means of aluminium. As it was beautifully crystallized, it was worth while to examine it more narrowly.

If violet perchloride of chromium be heated to redness in a glass tube with a fragment of aluminium wire, it is decomposed with incandescence; perchloride of aluminium is sublimed, and when the mass is treated with water, there remains an iron-gray metallic substance which consists essentially of aluminium and chromium.

This compound is obtained in a crystalline form in the following way:—The violet perchloride of potassium and chromium is prepared from bichromate of potash by heating it with an excess of concentrated muriatic acid, evaporating the green solution, and completely drying the mass. Or a mixture of 1 part of chloride of potassium and 2 parts of perchloride of chromium is prepared. Of this double salt a portion is thrown upon the bottom of a crucible, a fragment of aluminium is laid upon it, and this is again covered with the salt, which is pressed down a little. According to the formula to be given hereafter, $4\frac{1}{2}$ parts of the salt should be employed to 1 part of aluminium, but for the formation of crystals a certain excess of aluminium appears to be necessary. 1 part of aluminium is taken therefore to 2 parts of salt. The crucible is heated to redness in the charcoal fire, so that the mass just fuses; it is then cooled and placed in water, to extract the salt. The new compound remains in the form of a slightly coherent gray metallic mass, composed of fine, interlaced acicular crystals. To extract the excess of aluminium it is heated with solution of caustic soda, as long as any hydrogen gas is evolved. The crystalline powder is then well washed and dried. Sometimes, even when operating with small quantities, very beautiful crystals recognizable with the naked eye are obtained, but sometimes only a fine crystalline powder.

The crystals are of the colour of tin and have great lustre. They are partly square tables, and partly rectangular four-sided prisms with the terminal faces set on straight. When magnified 50 diameters, narrow truncations of the lateral and terminal edges were observed in some crystals, so that they had exactly the form of idocrase.

When heated to redness in the air, they change colour in the same way as steel, without becoming further oxidized. They are

not attacked either by solution of soda or by concentrated nitric acid. On the other hand, they are readily dissolved with a chrome-green colour by muriatic acid; evolution of hydrogen and formation of oxide of silicium take place. When the quantity is rather large, the oxide of silicium forms a filmy, snow-white mass, covering the surface of the fluid. After being washed and dried, this burns, when heated, as vividly as that prepared from the protochloride, hydrogen gas being suddenly evolved and burnt with explosion. Dry muriatic acid gas is readily decomposed by the compound when heated to redness, forming protochloride of silicium, white crystalline protochloride of chromium and perchloride of aluminium; the latter is sublimed.

The behaviour of this body to concentrated sulphuric acid is very remarkable. When heated therewith, it is oxidized to a green mass, but not with evolution of sulphurous acid; instead of this, there is a violent evolution of hydrogen gas and separation of free sulphur. It is probable that in this process sulphurous acid is produced at first, but that, as is the case with copper, a portion of this forms sulphate and sulphuret with another portion of the metal; the sulphuret then forms sulphuretted hydrogen with the water of the sulphuric acid. This, however, is not set free directly, because it is decomposed with the rest of the sulphurous acid into water and sulphur. At the same time it must be a consequence of the conditions of decomposition of the compound, that water is also decomposed and hydrogen set free.

This compound is very difficult of fusion, apparently more so than nickel. When fused, it forms non-crystalline, very hard and brittle masses of spec. grav. 4·9. These are not in the least acted upon by hot solution of soda; but if they contain free aluminium, by which they are scarcely rendered more fusible, they evolve hydrogen gas. But it is impossible to obtain a definite compound in this way even by operating upon the finest powder, as was proved by several discordant analyses.

In an attempt to fuse together into one mass various portions of the pulverulent compound with the addition of more of the double chrome salt and under a cover of white glass, the most violent coke fire only produced separate globules of the size of peas, with a very crystalline surface, a finely granular crystalline fracture, and great hardness. They were infusible, even in the spirit-flame, with oxygen gas. During solution in muriatic acid, it was evident that they contained a quantity of intermixed crystalline silicium, which remained in shining black laminæ, and was evidently due to the glass employed.

The analysis of this compound presented difficulties, inasmuch as it was not easy to obtain a sufficient quantity of it in pure crystals and free from excess of aluminium. It was effected by dissolving the substance in muriatic acid, separating the oxide of silicium (which, when formed in this way, is quite insoluble) by filtration, and weighing it, mixing the green solution with an excess of hydrate of soda and saturating it with chlorine gas. By this means

the oxide of chromium is very easily converted into chromic acid and the alumina separated. When the mass has acquired a pure yellow colour, it is heated to remove the excess of chlorine, and then mixed with carbonate of ammonia in order to destroy the hypochlorous acid, and precipitate any dissolved alumina. It is then again digested for some time, and the alumina separated by filtration and well washed. The chromic acid is then reduced to perchloride by muriatic acid and alcohol, and the oxide of chromium thrown down by ammonia. The analysis I. was made with the fused compound of spec. grav. 4·9; the analysis II. was made by Küpke with the crystalline compound. They gave—

	I.	II.
Chromium	63·00	63·05
Aluminium....	29·08	27·71
Silicium	4·37	5·03
Iron.....	3·30	2·61

The silicium and iron are derived from impurities in the aluminium employed; their quantities being increased in proportion as a part of the aluminium is lost as protochloride. They are too great to render it possible to deduce a probable formula from the above numbers. If the iron and silicium be deducted as non-essential, there remain chromium and aluminium in the relative centesimal proportions of 68·4 : 31·6. A compound $=AlCr$ would require 66·08 of chromium and 33·92 of aluminium. On the other hand, it might be that silicium formed an essential constituent of this compound, for on careful examination it appeared that even well-developed, strongly lustrous crystals yielded a portion of oxide of silicium when dissolved. If, therefore, we regard the iron as truly non-essential, but as partially and isomorphically, replacing alumi nium or chromium, we might deduce from the above numbers, and as most nearly agreeing therewith, the formula $Al^{11} Cr^{12} Si$ (or perhaps $AlSi + Al^{10} Cr^{12}$), which requires—

Chromium.....	65·0
Aluminium	30·6
Silicium.....	4·4

This, however, is not very probable, and is only an expression of the existing analysis of this body.—*Nachrichten der Kön. Gesellsch. der Wissensch. zu Göttingen*, 1858, p. 78.

Alloys of Zinc, Tin, and Lead. *By* J. W. Slater*.

The following alloys of zinc, tin, and lead were formed and examined under my direction by Mr. W. Sharman, one of my pupils.

a. Tin, 16 parts; zinc, 4 parts; lead, 4 parts.

b. Tin, 16 parts; zinc, 3 parts; lead, 3 parts.

These alloys appear to possess very valuable properties, and will probably to a considerable extent supersede the various "Britannia metals," "white metals," and pewters now in use. They can be

* Communicated by the Author.

rolled and "spun" with ease, and are well adapted for counter-covers, publican's tankards, ink-stands, &c.

In the preparation of these alloys, which differ from all similar compounds on record chiefly by the much larger per-centage of zinc employed, the following precautions must be observed.

The zinc is melted first, at as low a heat as possible, the tin is next added, and finally the lead. The whole is well stirred up with a green wood pole to ensure perfect mixture, and to prevent oxidation, for which latter purpose a coating of borax and the addition of a little resin will be found useful. The whole operation should be conducted as quickly as possible, and all excess of heat should be most carefully avoided.

The proportions of the ingredients may be modified according to the purpose in view. The zinc may be augmented where less ductility is required, and the tin increased where flexibility and a better colour are requisite. For tea-pots, &c., the alloy *b* is preferable.

These metals being easily fusible, a due care must be taken in the selection of the solder.

They do not appear to tarnish more readily than the ordinary white metals, and are very considerably cheaper.

Our reason for laying the whole process in this manner before the public, is that a patent, of which these alloys were to form the subject, was rendered worthless by the dishonesty of an individual who had been admitted to an interest therein.

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of Sugar. *By* H. Fehling.

Three principal methods are employed in the determination of sugar in organic substances; the fermentation process, the test by means of polarization, and the test with a standard alkaline solution of alkaline tartrate of copper. None of the methods give an absolutely exact result, but the author after numerous experiments regards the third as that which furnishes the most accurate and certain results.

With both grape-juice and solutions of pure cane-sugar, it is not easy to obtain in a short time a fluid perfectly free from sugar by fermentation; even after the lapse of eight days there is still undecomposed sugar; and, moreover, there is now no doubt that in the fermentation there is a formation not only of carbonic acid and alcohol, but also of other products, such as amylic and butylic alcohols, &c., and even of succinic acid, according to Pasteur*. Under these circumstances the carbonic acid is no certain measure of the sugar.

The optical test is often rendered tedious on account of colouring matters, but even with readily decolorizable beetroot-juice, con-

* Chem. Gaz. page 126 of the present volume.

taining 10 to 14 per cent. of sugar, the author has never found it possible to determine the amount of sugar within $\frac{1}{4}$ per cent., or $\frac{1}{40}$ to $\frac{1}{56}$ of the entire quantity of sugar. With grape-sugar the error due to the uncertainty regarding the uniformity of the colours is still greater, because it deviates the light less than cane-sugar. It often happens that different persons, in consequence of a dissimilar appreciation of colours, obtain results differing by a constant amount. It is, moreover, still uncertain how far the rotatory power, for example, of diabetic sugar is altered by the presence of foreign bodies, temperature, &c.

For the determination of grape-sugar, the reduction of solutions of copper furnishes the most accurate and concordant results, when certain precautions are observed. It has been particularly objected against this method that other matters may also act in the same way as sugar; this objection applies equally to the optical test. Most foreign bodies may be removed by precipitation with basic acetate of lead, for which reason this purification is usually essential. In *normal* urine which had been mixed with 10 to 20 per cent. of grape-sugar (prepared from urine or honey, according to analysis $=C^{12}H^{12}O^{12}$), the author has always found exactly the added quantity of sugar after treatment with basic acetate of lead. As the lead precipitate after drying occupies a very small volume, the saccharine fluid is diluted with water and basic acetate of lead to the proper volume, and after precipitation a portion of the supernatant fluid is rapidly filtered and then employed.

A further essential condition is the constitution of the solution of copper. The author has already shown that this must have a definite composition, in order that it may not decompose spontaneously when boiled. The purity of the tartrate of potash appears to have a particular influence upon this, and for this reason the author has employed in place of neutral tartrate of potash, the more readily crystallizable tartrate of potash and soda (Rochelle-salts). The solution of copper may be kept for years in well-closed and completely filled bottles; in partly emptied or badly-closed vessels it readily attracts carbonic acid, and then separates red protoxide of copper when boiled. The solution undergoes the same alteration when carbonic acid is passed into it, or any other acid is added by which a portion of the alkali is saturated. If the altered solution be mixed before boiling with a dilute alkaline solution instead of pure water, it is unaltered by boiling. The solution of copper must therefore be rendered strongly alkaline and kept from contact with carbonic acid; the fluid to be tested for sugar also must not be acid, unless the copper solution contains a great excess of alkali.

The author has found it the best plan to keep the solution of copper gently boiling over a lamp and add the saccharine solution so slowly as scarcely to interrupt the ebullition. By adhering to the process described with solutions containing 15—20 per cent. of grape-sugar, the results obtained, even by different experimenters, do not differ more than 0·1 per cent., so that they agree within $\frac{1}{150}$ or $\frac{1}{200}$ of the amount of sugar.

The most certain results are obtained with grape-sugar; cane-sugar must first be converted into fruit-sugar by heating with dilute acids, in which case it is difficult to recognize the completion of the conversion. Sugar of milk is more readily converted into glucose than cane-sugar by boiling with dilute sulphuric acid; but this is unnecessary, as sugar of milk itself reduces peroxide of copper to protoxide, although in a different proportion from grape-sugar. 1 equiv. of sugar of milk reduces 7 equivs. of peroxide of copper according to Rigaud, Städeler, and Krause, 7·5 equivs. according to Bödeker. As much as 12 years ago the author attempted to value the solution of copper by means of sugar of milk, but could not obtain any constant result. He has since made experiments upon the quantity of the copper-salt reduced by boiling an accurately weighed portion of sugar of milk with a slight excess of the solution of copper, separating the protoxide of copper by filtration and determining its exact quantity. By this means the calculation always gave *more than* 7 equivs., sometimes even more than 8 equivs. of peroxide of copper; in six experiments with the same normal solutions of sugar of milk and sulphate of copper, Dr. Mark obtained to 1 equiv. of the former from 7·62 to 7·96 equivs. of the copper-salt. The duration of the boiling appears to have a decided influence upon the result. For the determination of sugar of milk, therefore, it is undoubtedly necessary to convert it into glucose by boiling with sulphuric acid; this is soon effected so completely that 1 equiv. of sugar decomposes exactly 10 equivs. of the copper-salt.—Liebig's *Annalen*, April 1858, p. 75.

On the Determination of Nitric Acid. *By* R. Fresenius.

The method of Pelouze for the determination of nitric acid, furnishes sometimes good and sometimes erroneous results, even when carried out with the greatest care. In this all agree who have occupied themselves with the examination of this method, such as F. Mohr, Abel, and Bloxam. The experiments made in the author's laboratory long since led him to the same result.

The causes of the want of accuracy are as follows:—

a. In the first place, the action of air upon the nitrous oxide gas present in the flask together with aqueous vapour, by which nitric acid is regenerated.

b. Incomplete expulsion of the nitrous oxide from the fluid, in consequence of which it reduces a larger quantity of solution of mineral chameleon than corresponds with the amount of protoxide of iron contained in it. This is only to be feared in dilute solutions.

c. Evolution of nitric acid before it has acted upon the protochloride of iron; this is to be guarded against when the fluid boils very rapidly after the addition of the nitrate, and when the excess of protochloride of iron is proportionally small.

d. Perhaps also sometimes loss of iron by careless boiling; this is especially to be feared when a portion of the protochloride and

perchloride of iron is deposited in a solid form on the top of the fluid.

The author has modified the method of Pelouze, so as to avoid all these sources of error and obtain perfectly satisfactory results. A tubulated long-necked retort capable of containing about 200 cub. cent., is fixed so that the neck is directed a little obliquely upwards. Into its belly is put about 1·5 grm. of fine pianoforte wire (accurately weighed), and from 30 to 40 cub. cent. of *pure* fuming muriatic acid are added. Hydrogen gas, washed in solution of potash, is now passed in through the tubulature by means of a glass tube only reaching about 2 centims. into the retort, and the neck of the retort is united to a U-shaped tube containing a little water. The belly of the retort is placed on the water-bath and gently heated until the iron is completely dissolved. It is then allowed to cool in the current of hydrogen, which is afterwards strengthened, and the nitrate weighed in a small tube is thrown in, with the tube through the neck of the retort. The quantity of the nitrate should be calculated so that it may only contain about 0·200 grm. of nitric acid. After the union of the neck of the retort with the U-tube, the contents of the retort are heated in the water-bath for about a quarter of an hour; the water-bath is then removed, and heat is applied by the lamp so as to produce strong ebullition until the solution, which has a dark colour from the absorbed nitrous oxide gas, has acquired the colour of perchloride of iron; after reaching this point, the boiling is continued for a few minutes. Every time the fluid is agitated, care must be taken that dry salt is never deposited on the walls of the retort. Before the boiling is stopped, the current of hydrogen gas is strengthened in order to prevent the entrance of air through the U-tube when the lamp is removed. The retort is allowed to cool in the current of hydrogen, the contents are much diluted with water, and finally, the iron still existing as protoxide is determined with solution of permanganate of potash.

The following determinations were effected by this process:—

	1.	2.	3.	4.
Iron put into the retort	1·1223	1·5950	1·4403	1·3722 grm.
Nitrate of potash put into the retort	0·3742	0·2693	0·2585	0·2454 „
Solution of permanganate of potash used	62·35	78·05	68·75	65·45 c. c.
100 of solution of permanganate of potash corresponded to iron	0·8010	1·470	1·470	1·470 grm.

Instead of 100 of nitrate of potash the experiments gave—

1.	2.	3.	4.
100·1	100·03	100·03	100·57

This method may therefore be employed with the greatest confidence, of course only when no organic matters are present.—Liebig's *Annalen*, May 1858, p. 217.

THE CHEMICAL GAZETTE.

No. CCCLXXX.—August 16, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Identity of Anchoic Acid with Lepargylic Acid.

By G. B. Buckton, *Esq.*, *F.R.S. &c.**

M. Wirz has lately described in Liebig's 'Annalen'†, under the name of lepargylic acid, a crystalline substance which he has procured by acting upon some of the fatty bodies, resulting from the distillation of cocoa-nut oil with concentrated nitric acid.

The author of the present notice wishes to call attention to the circumstance, that a substance possessing exactly the same characters and properties, has been already fully described by him in the Transactions of the Chemical Society‡, under the name of anchoic acid.

As a translation of M. Wirz's paper has appeared in the Chemical Gazette (p. 247), it may not be out of place here very briefly to recapitulate the conditions under which anchoic acid occurred to the author, and also state his claims to priority in its isolation.

When the substance known in commerce as Chinese wax, the secretion of an insect (*Coccus pela* of Westwood), is digested with nitric acid of the specific gravity 1·40, the crystalline compound is slowly converted into a variety of bodies, which may be conveniently classified,—first, into volatile acids which distil with more or less facility at 100° C. in conjunction with aqueous vapour; secondly, fatty and oily substances which are insoluble in water; and lastly, acids which remain in the condition of a syrup, and which are soluble in water.

By fractionizing the distillate and preparing the barium salts in a manner detailed elsewhere, the volatile products were found to consist chiefly of butyric, caprylic, and œnanthylic acids, together with a distinct, but small portion of hydrocyanic acid. The fatty and oily bodies insoluble in water were not examined.

The remaining syrup, soluble in water, was separated from oily flakes by filtration through asbestus, and the solution was concen-

* Communicated by the Author. † Liebig's Annalen, civ. p. 257.

‡ Quart. Journ. Chem. Soc., vol. x. p. 166.

trated, water being occasionally added to facilitate the removal of the nitric acid.

Crystalline pellicles formed when the liquid was set aside for some hours, which were successively removed until they ceased to appear when the syrup was further reduced in bulk by evaporation.

The first crops of crystals were well washed with cold water, melted, and powdered. Afterwards a little æther was used to remove oily traces, and finally, a crystallization from hot water yielded the acid in nodules of a snowy whiteness.

Analysis gave numbers which pointed to the formula

$$C^{18} H^{16} O^{8},$$

which is the same as that given by Wirz to his acid.

The substances analysed were,—

Anchoic acid	$C^{18} H^{16} O^{8}$
Anchoate of silver	$C^{18} H^{14} Ag^{2} O^{8}$
Anchoate of barium	$C^{18} H^{14} Ba^{2} O^{8}$
Acid anchoate of potassium	$C^{18} H^{15} K O^{8}$.

The melting-point of anchoic acid was found to be 237°—240° F. Wirz found that lepargylic acid melted at 239°—255° F. Both acids crystallize from water in soft nodular masses.

They also agree in their greater solubility in æther and their less solubility in water, when referred to suberic acid; and in fine, their several descriptions accord so well, that nothing more seems requisite to prove their identity.

An examination of the mother-liquid after removal of anchoic acid, showed the presence of at least two of the lower members of the series $C^{2n} H^{2n-2} O^{8}$. Suberic acid is one of these, and perhaps the chief product of the decomposition of Chinese wax by nitric acid. The proportion in which it occurs seems to depend mainly on the duration of the action and the concentration of the nitric acid employed. The greater solubility of suberic acid in water furnishes the best method for separating it from anchoic acid.

The strongly acid mother-liquid still retained in solution a crystalline substance which melted at a temperature of 230° F. By analysis it indicated the formula

$$C^{14} H^{12} O^{8},$$

which is that of pimelic acid, a substance previously obtained by Laurent from the oxidation of bees'-wax, spermaceti, and other fatty bodies by nitric acid.

After the above-mentioned crystalline bodies had been removed from the nitric acid solution, there yet remained a soft and tenacious mass, which although of a greasy nature was perfectly soluble in water.

As this mass was clearly a mixture of various bodies, and no crystalline salts could be formed, a further separation was not attempted, since no adequate return was promised for the sacrifice of time and labour. An extended search perhaps was the less necessary, since both Malaguti and Laurent have investigated in the same direction.

In conclusion, it may be remarked that this series of the bibasic acids is now complete from oxalic to sebacic acid, with the exception of the terms containing six and ten equivalents of carbon. Pyrotartaric acid cannot be considered as representing a member of this group.

On the Products of the Action of Chlorine upon Paraffine. *By* P. Bolley.

The author gives the following account of his investigation of the action of chlorine upon paraffine, but states that an extended preliminary investigation of the nature of the bodies which we usually call paraffine must be made, before a clear insight into the decompositions effected by chlorine can be attained. From the investigations of its discoverer, von Reichenbach himself, as from those of Malaguti, Hofstädter, Fillipuzzi and others, the paraffines, whether natural or artificial, are generally mixtures of isomeric, solid hydrocarbons of the formula $C^n H^n$, which may be decomposed by solution in alcohol, and separation of the more soluble portion from the less soluble, into bodies of various crystalline forms, specific gravities, and melting-points. The lowest melting-point (observed by Laurent in a natural paraffine) is 91°·4 F.; the highest is probably that observed by Hofstädter in a portion of natural paraffine from Galicia obtained by fractional distillation, of 149°·9 F. Hofstädter gives the melting-point of Reichenbach's paraffine obtained from beech-wood tar at 117°·5 F. The author obtained from Professor E. Schweizer a small quantity of paraffine which had been long before presented by Reichenbach to a collection of preparations in Zurich; he found its melting-point to be 110°·3 F. Most of the commercial paraffine is not pure; it either contains stearic acid, which is necessary for the manufacture of candles, or it has not been perfectly freed from foreign substances. Paraffine procured from Bonn, required repeated treatment with caustic soda and sulphuric acid until it was no longer acted upon. After this treatment its melting-point was 122°·9 F.

It is universally stated that paraffine is not acted upon by chlorine. At the ordinary temperature, indeed, no action takes place, but it does not long resist when it is rendered fluid by heat, and chlorine is then passed through it. Bubbles of hydrochloric gas are immediately observed escaping; the mass soon becomes so changed that it remains thickly fluid even at ordinary temperatures; but the state of semifluidity does not persist when the passage of the chlorine is long-continued, the mass, on being cooled, passing rather back to the solid form and appearing, even when heated to 212° F., more and more tenacious, so that its contact with the gaseous chlorine is much obstructed The following circumstances must be especially indicated as very much against the determination of the composition of the products of various stages of decomposition.

1. Nothing is to be detected in the physical character of the more or less chlorinated mass that can lead to the conclusion that these are products of a constant composition. There are no changes of colour, nor are any separations of definite forms to be recognized. After the mass has taken up some chlorine it appears amorphous, and retains its original aspect without any alterations, except those already mentioned in its consistence. The comparative solubility also furnished no means of detecting and separating the different substances in the mixture.

2. It is extremely difficult to expel the hydrochloric acid formed completely by heating the tough paste; standing for days in the water-bath is not sufficient for this purpose, the odour always occurring again when the hot mass is stirred. By solution in alcohol and evaporation, a mass with less odour of muriatic acid is obtained, but this, from its obstinately retaining an odour of alcohol, raises apprehension of impurities of a different kind.

3. The difficulties in the way of obtaining a compound completely saturated with chlorine are not less than in procuring characteristic intermediate products, because, as already stated, the consistence of the mass is very obstructive to the reception of chlorine.

Several analyses were made of the products of different stages of the reaction of chlorine. The amounts of carbon and hydrogen were determined either with chromate of lead or with oxide of copper and oxygen gas with metallic copper inserted in the anterior extremity of the combustion-tube; the chlorine was determined by heating with soda-lime, dissolving the latter in nitric acid, and precipitating with solution of silver. Some of the analyses gave—

	I.	II.	III.
C	55·200	39·368	34·500
H	8·257	5·297	4·192
Cl	36·290	54·801	61·424

If these numbers be divided by the equivalents of carbon, hydrogen, and chlorine, and the values obtained calculated on the assumption that the carbon in all three =1000, which is the simplest plan, as we are unacquainted with the equivalent of paraffine, they give—

in I.			II.			III.		
1000	equivs.	C	1000	equivs.	C	1000	equivs.	C
896	„	H	807	„	H	728	„	H
111	„	Cl	229	„	Cl	301	„	Cl

From this it appears at least that in these compounds hydrogen is displaced by chlorine; and indeed the simplest expression for the three products would be $C^{10} H^{9} Cl$, $C^{10} H^{8} Cl^{2}$, and $C^{10} H^{7} Cl^{3}$. It must be added to these results of the analyses, that a considerable series of other determinations of the three elements were made, which, when calculated as above, led to less simple expressions, but in by far the majority of cases they may be arranged in a series in which the decrease of hydrogen corresponds with a nearly equal

increase of chlorine. But in nearly all the analyses, as in the above, there is more chlorine and hydrogen found than corresponds with the formula $C^n H^{n-x} Cl^x$; this is due to adhering chlorine and hydrochloric acid.

In this investigation it remains quite unexplained how a particular solid hydrocarbon of the series of homologues $C^n H^n$ would behave towards chlorine. The fruitlessness of the attempts to prepare compounds possessing individual, physical or chemical properties, will, in the author's opinion, exist as long as we are not in a condition to separate the different paraffines from their mixtures. He was soon convinced that little advantage would be derived from the investigation in this direction; but he nevertheless continued it further, because another view as to the products presented itself. "Chloraffine," as a paraffine saturated as much as possible with chlorine may be termed for brevity, is an amorphous body, limpid when freed from all moisture, fusible by a gentle heat, but hard at a low temperature, and heavier than water, which has the greatest resemblance to a resin, such as copal, or, when heated, to balsam of copaiva. It is tolerably soluble in benzine, and the solution may be readily spread upon paper, wood, &c. After the evaporation of the benzine, the paper becomes extraordinarily transparent, more so perhaps than by any other means. It may be marked with a lead-pencil, and has not the least greasiness, but always retains a certain, although very slight stickiness. As the tenacity increases with the amount of chlorine, it is not improbable that by the energetic action of chlorine a perfectly hard and brittle compound may be obtained, which may be separated in a perfectly dry state from its solution in benzine. Whenever this is the case, the technical application of these products will soon follow.—Liebig's *Annalen*, May 1858, p. 230.

On the Compound of Aldehyde with Anhydrous Acetic Acid. *By* Dr. A. Geuther.

In a previous memoir*, upon the assumption that the compounds prepared by Wicke by the action of chlorobenzole ($C^{14} H^6 Cl^2$) upon the silver-salts of acetic acid, benzoic acid, &c. are *true* æthers of the supposed bibasic benzolic alcohol, the author expressed the opinion that perhaps the acetic æther of the glycolic alcohol is to be regarded as a compound of aldehyde with anhydrous acetic acid. He has since succeeded in combining aldehyde directly with anhydrous acetic acid. The product, however, is not the acetic glycolic æther of Wurtz, but a body isomeric therewith, the boiling-point of which is 335°·8 F., or about 36° F. lower than that of the former.

If 1 equiv. of pure aldehyde and 2 equivs. of anhydrous acetic acid ($C^4 H^3 O^3$) be enclosed in a tube and heated in the oil-bath to 356° F. for about twelve hours, the mixture usually becomes brown, probably from the secondary action of a trace of oxychloride of phosphorus, which the anhydride still retained. On opening the

* See Chem. Gaz., vol. xvi. p. 267.

tube and rectifying the contents, uncombined aldehyde and acid are obtained, together with a fluid which boils at a higher temperature. The boiling-point rises suddenly from 284° F. to 320° F., and at 338° F. the last portions usually pass. If the product passing above 284° F. be washed with hot water, in which it sinks in an oleaginous form, the last traces of the anhydride are removed, and a product is obtained, which when dried over chloride of calcium, has a constant boiling-point of 335°·8 F. (corrected). It has a mingled odour of onion and smoke; has an acid reaction, probably from slight decomposition during distillation; it is not very stable when heated, and appears to be gradually decomposed by repeated rectification. When heated with hydrate of potash it becomes brown, and furnishes the same peculiar odour given by aldehyde alone with hydrate of potash; acetate of potash is formed. Caustic baryta has no decomposing action; but if a little water be added, the same action takes place as with hydrate of potash, and acetate of baryta is formed. With the addition of an excess of ammonia and the assistance of heat it reduces nitrate of silver, producing gray metallic silver.

Glacial acetic acid, treated in the same way with aldehyde, furnishes no compound.

Analysis gave,—

	Calculated.	Found.		
		1.	2.	3.
C^{12}	49·32	48·99	50·81	49·82
H^{10}	6·85	6·96	6·74	6·96
O^{8}	43·83			

The substances analysed were from two different preparations; 2 was not washed with water, but obtained by simple rectification; 3 is the same substance (2), purified by washing with hot and cold water, and distilled.

Aldehyde also appears to combine with anhydrous benzoic and succinic acids.

Of other aldehydes belonging to the acetic acid series, the author has endeavoured to combine œnanthole; heated to 500° F. in the oil-bath with anhydrous acetic acid, this gave no satisfactory results on rectification, as from the great heat at which the distillation required to be effected, the compound was again decomposed.

Oil of bitter almonds may, however, be combined with anhydrous acetic acid in the above way; when heated to 446° F. it furnishes a thin oil insoluble in water, which is probably the compound prepared in another way by Wicke, and regarded by him as acetic benzolic æther.

Even by employing perfectly pure materials, the author did not succeed in combining acetone with anhydrous acetic acid. After being heated for a long time to 410° F., the two substances were always uncombined in the tube.

Thus a proof is furnished of a possible series of compounds isomeric with the glycolic alcohols. In his previous memoir the author

set up the formula $\frac{(C^2 H^4, C^2 O^2) HO}{HO}$ for glycolic alcohol, but he does not now consider that this agrees with it, but that it must be regarded as $\frac{(C^4 H^2, H^2 O^2) HO}{HO}$, as is shown also by its behaviour to perchloride of phosphorus, in which protochloride of elayle is formed, and not the product formerly described by him.

Acetate of aldehyde. $(C^2 H^4, C^2 O^2) \left\{ \begin{matrix} C^4 H^3 O^3 \\ C^4 H^3 O^3 \end{matrix} \right.$

Acetic glycolic æther. $C^4 H^2, H^2 O^2 \left\{ \begin{matrix} C^4 H^3 O^3 \\ C^4 H^3 O^3 \end{matrix} \right.$

He remarks in conclusion, that the product formerly described by him obtained from aldehyde and perchloride of phosphorus, boils exactly at 137°·66 F. He adds, that when metaldehyde is heated in closed tubes for a long time to 366° F., it is again converted into ordinary aldehyde.—Liebig's *Annalen*, May 1858, p. 249.

Investigation of Veratric Acid. *By* M. Merck.

The author obtained a small quantity of veratric acid as an accessory product in the preparation of veratrine from the seeds of *Sebadilla*. To ascertain whether it was the same acid examined by Schrötter*, he analysed it and obtained the following results:—

	Experiment.		Theory and formula of Schrötter.
C	58·74	C^{18}	59·34
H	5·62	H^{10}	5·49
O	35·64	O^8	35·17

The analysis of the silver-salt gave 37·76, 37·59, and 37·81 per cent. of metallic silver. Theory requires 37·36 per cent. These determinations agree perfectly with Schrötter's formula $C^{18} H^{10} O^8$.

Veratric acid dissolves in monohydrated nitric acid; on the addition of water, *nitroveratric acid* is thrown down. This is but slightly soluble in water, but dissolves readily in alcohol, and crystallizes in small yellow scales. When heated above 212° F. it fuses and becomes decomposed. It contains—

	Found.			Calculated.
C	47·14	47·34	47·43	47·57
H	4·68	4·50	4·42	3·96
N	..	..	6·78	6·16

These analyses lead to the formula

$$C^{18} H^9 N O^{12}.$$

When mononitroveratric acid is boiled with concentrated nitric acid, a second equivalent of hydrogen may be replaced by nitrous

* Liebig's Annalen, xxix.

vapour, but the binitroveratric acid thus formed is difficult to separate from the mononitro-acid.

Chlorine and bromine react very energetically upon veratric acid, but the products of substitution formed in these reactions are uncrystallizable, of a pasty appearance, and not adapted to further examination.

Perchloride of phosphorus does not appear to react upon veratric acid.

When this acid is mixed with three times its weight of baryta, and the mixture is gently heated in a retort, a very brisk reaction takes place, and an oleaginous colourless body distils over. This body, which the author names *veratrole*, possesses an agreeable aromatic odour, a density of 1·086 at 41° F., boils between 396° and 401° F., and becomes solid at 59° F. It is neutral towards the alkalies and weak acids. It contains—

	Found.	Calculated.
C	69·49	69·56
H	7·70	7·24
O	22·81	23·20

These numbers agree with the formula

$$C^{16} H^{10} O^4.$$

In the operation which gives rise to the formation of veratrole, veratric acid loses 2 equivs. of carbonic acid.

Veratrole is strongly acted on by concentrated nitric acid. In this reaction mononitroveratrole is first formed, and when the action of the acid is long continued, binitroveratrole. The analysis of the latter gave—

	Found.			Calculated.
C	41·22	42·31	42·22	42·10
H	3·46	4·02	3·96	3·51
N			11·69	12·28

Bromine reacts energetically upon veratrole; hydrobromic acid is evolved, leaving a crystalline mass from which the bibrominated compound may be obtained by repeated crystallization. Bibromoveratrole is insoluble in water, but dissolves readily in alcohol and in æther. The latter deposits it in fine prismatic crystals. These fuse at 198° F., and become volatilized without alteration at a higher temperature. It contains 54·17 per cent. of bromine; the formula $C^{18} H^8 B^2 O^4$ requires 54·04 per cent.

The continued action of bromine upon veratrole gives origin to products of substitution which contain more bromine, but which do not crystallize. Chlorine reacts in the same way; a crystalline mass is first formed, and subsequently a pasty mass.

Perchloride of phosphorus has no action upon veratrole, nor has muriatic acid. Potassium, when put into it, becomes surrounded by a gelatinous mass, without any observable evolution of hydrogen. Bisulphite of soda and nitrate of silver have no action upon veratrole.—*Comptes Rendus*, July 5, 1858, p. 36.

On the Action of Potash upon Wool. *By* C. GREVILLE WILLIAMS*.

Several years ago I made a variety of experiments on the action of heat upon certain proteine compounds. I distilled feathers *per se*, and found the distillate to contain, in addition to large quantities of pyrrol, certain volatile bases. In consequence of the non-employment of an alkali, the proportion of bases in the distillate was much less than it would otherwise have been. I observed also that a sulphuretted gas was evolved which rapidly reacted upon peroxide of lead, great heat being at the same time evolved. Since then it has been stated by Limpricht and Schwanert† that horn yields pure amylamine on distillation with potash; this fact appeared to me so interesting, and so much opposed to the ideas I had previously formed of the complicated reaction undergone by albuminous bodies under the influence of heat, with or without the presence of alkalies, that I was induced to repeat my experiments. The following is an account of a preliminary experiment undertaken with this view.

As I could not conveniently procure feathers, I resorted to wool as being of a texture easily acted on by potash. A solution of potash of moderate strength was heated to boiling in an iron pan, and pieces of flannel added. They dissolved almost immediately; some cotton threads accidentally present, remaining insoluble, were removed with a rod. As the fluid becomes concentrated it froths violently, but the heat being so regulated as to prevent the materials from overflowing, the whole gradually acquired a peculiar consistency, so that it could be moved in one mass with the rod. Large quantities of ammonia were evolved together with the smell of an alcohol base. The odour was by no means offensive, the whole of the sulphur being retained by the potash. At this point the mass was transferred to an iron still. The distillate was received in hydrochloric acid. The acid solution was then evaporated in order to remove the greater portion of the sal-ammoniac by crystallization. The whole of the mother-liquids were evaporated to dryness, and the mixed salts treated with strong alcohol to dissolve the chlorides of the volatile bases. The alcoholic solution was then evaporated to dryness, and the operation repeated. The purified chlorides, after being heated gently to remove the last traces of alcohol, were dissolved in a little water. On the addition of solid potash an oil made its appearance; it was separated, dried by repeated digestion with sticks of potash, and distilled. It came over between 80° and 100° (176° to 212° F.). This boiling-point, coupled with the odour, led me to suspect a mixture of butylamine and amylamine. The oil was dissolved in hydrochloric acid, and bichloride of platinum added. A crop of brilliant golden-yellow crystals, resembling crystallized iodide of lead, soon made their appearance. The following is the result of a platinum determination:—

0·1756 grm. gave 0·0586 of platinum;

* Communicated by the Author. † Chem. Gaz. 1857, pp. 203 and 351.

or, per cent.,

Experiment.	Theory $C^{10}H^{13}N, HCl, PtCl^2$.
33·37	33·73.

The base was therefore amylamine, with which the number obtained closely agrees. The mother-liquid of the above crystals on careful evaporation gave another crop, which was analysed as follows:—

0·2144 grm. gave 0·0760 platinum.

Experiment.	Theory $C^8H^{11}N, HCl, PtCl^2$.
35·45	35·42.

It is plain from the above numbers that flannel yields by distillation with potash a mixture of at least two bases, namely butylamine and amylamine. It is very possible that others are also present in too small a quantity for isolation in working on so small a scale. I shall seize the first opportunity of making an experiment on a very large quantity of material, in order to determine this question, which is interesting in more than one point of view. This is the first time that butylamine has been found in products of distillation since the discovery of petinine in bone-oil.

It has been shown by Limpricht that alanine yields ethylamine, and leucine amylamine by distillation with potash; the decomposition undergone is, however, too complex to be represented in an equation, unless it be justifiable, as he appears inclined to think, to consider the ammonia, empyreumatic oils, &c. as mere secondary products. If we allow this, a very interesting consequence flows from this mode of production of butylamine, namely, that flannel by proper treatment might be made to yield one of the missing homologues of leucine. This will appear on examination of the following Table:—

Glycocoll	C^4	H^5	NO^4	$-C^2O^2=$	C^2	H^5	N	Methylamine.
Alanine	C^6	H^7	NO^4	C^2O^4	C^4	H^7	N	Ethylamine.
Unknown	C^8	H^9	NO^4	C^2O^4	C^6	H^9	N	Propylamine.
Unknown	C^{10}	H^{11}	NO^4	C^2O^4	C^8	H^{11}	N	Butylamine.
Leucine	C^{12}	H^{13}	NO^4	C^2O^4	C^{10}	H^{13}	N	Amylamine.

If the flannel be distilled without the addition of potash, an intolerably fœtid oil comes over, accompanied by crystals of carbonate of ammonia, large quantities of pyrrol, and torrents of sulphuretted hydrogen holding in suspension traces of bisulphide of carbon. The clothes acquire and retain for days an odour of the most offensive kind. The operation, conducted in this manner, yields scarcely more than traces of basic oil, almost the whole of the nitrogen appearing to be converted into ammonia.

On the Behaviour of Copper in Hydrochloric Gas.

By F. Wöhler.

If copper wire or copper foil be moderately heated (to a red heat, such as a glass tube will bear) in hydrochloric gas, protochloride of

copper is formed and hydrogen is set free. The protochloride of copper is colourless and transparent, and flows down, during the operation, into the depressed part of the tube. As far as the tube is brought to a red heat, its inner wall is converted into protoxide of copper glass, of a fine dark red colour.—Liebig's *Annalen*, cv. p. 360.

ANALYTICAL CHEMISTRY.

On the Discrimination and Separation of Arsenic from Antimony and Tin. *By* R. Bunsen.

I. *Qualitative determinations.*

The three oxides of antimony may be most easily and certainly distinguished by their behaviour towards hydriodic acid and ammonio-nitrate of silver. Antimonic acid and antimoniate of antimony, even when they have been previously strongly heated, dissolve in muriatic acid when gently heated, producing, after the addition of a little iodide of potassium, a dark brown solution in consequence of the separation of iodine, which remains dissolved in the excess of iodide of potassium; oxide of antimony, on the contrary, is dissolved by the acid to form a pale yellow fluid, without any separation of iodine. As the only iodide of antimony is that corresponding with the oxide (SbO^3), and there is none corresponding with antimonic acid (SbO^5), SbI^3 and I^8 are produced in the former case, and in the latter only SbI^3. If the quantity of antimonic acid dissolved be not too small, violet fumes appear during the ebullition of the fluid. But even when the quantity to be detected is not more than a few hundredths of a milligramme, it is sufficient to agitate the somewhat dilute solution with a few drops of sulphuret of carbon, to produce the violet blue or amethyst-red colour of iodine. As a matter of course only muriatic acid free from chlorine, and iodide of potassium containing no traces of iodate of potash, must be employed in these experiments.

Antimonic acid (SbO^5) and antimoniate of antimony (Sb^3O^8) may therefore be easily distinguished from oxide of antimony (SbO^3) by this reaction. To distinguish the two former from each other, the ammonio-nitrate of silver may be employed. The oxide of silver in this salt is reduced by oxide of antimony, whether free or combined with antimonic acid, to form black protoxide of silver. If therefore the oxide to be tested be triturated with water to form a milky drop, and dried upon a porcelain saucer, a deep black spot is obtained as soon as the above mentioned silver-salt is poured over the place covered with the dull coating of oxide of antimony, and gently heated. By the same reaction also the arsenical and antimonial spots obtained by Marsh's process, may be distinguished from each other with great certainty. If nitric acid of spec. grav. 1·42 be dropped upon such an antimonial spot produced in a porcelain saucer, so that the spot may be completely moistened by the

acid, the former disappears in a short time when a gentle heat is applied. If, while the saucer is heated from below by a lamp, the acid moistening the spot be blown upon so strongly that it evaporates without boiling, the white coating remaining in the place of the evaporated fluid consists principally of oxide of antimony, which produces a deep black spot of protoxide of silver when ammonio-nitrate of silver is dropped upon it. If, on the contrary, the spot consisted of arsenic, the same treatment would furnish the well known yellow precipitate of arsenious acid or the brownish-red precipitate of arsenic acid, according as the acid was previously allowed to act for a longer or shorter time upon the spot. If arsenic or antimony, or both, have to be detected in the presence of tin, they are separated by the method hereafter described, and tested by means of the above mentioned reaction with ammonio-nitrate of silver.

II. *Quantitative separations.*

As regards the determination of antimony, in the first place, this is best weighed in the form of antimoniate of antimony, $Sb^2 O^8$, as this oxide is neither volatilizable nor decomposable by ignition in the air. As antimony is almost always separated in analyses in the form of sulphuret, the principal point is to find a simple and sure method for the conversion of this sulphuret into antimoniate of antimony. If nitric acid of spec. grav. 1·42 be employed for this purpose, very erroneous results are obtained. It is scarcely ever possible, by means of this acid, to convert the oxide of antimony formed, completely into antimonic acid, so that during calcination there is danger of a considerable loss by the volatilization of sulphate of antimony. Moreover, the boiling-point of the acid, which is nearly 18° F. above the melting-point of sulphur, causes the sulphur separated during the oxidation to melt into drops which resist oxidation with the greatest obstinacy, and exert a decomposing action upon the oxide already formed, during the calcination of the oxidized mass. All these disadvantages may, however, be readily avoided by employing fuming acid, the boiling-point of which is 187° F., and consequently below that of sulphur. If sulphuret of antimony be treated with 8 or 10 times its quantity of such acid in a weighed porcelain crucible with a concave cover, the sulphur separates in a finely divided state, which is easily and completely oxidized when the acid is slowly evaporated in the water-bath. The white mass remaining in the crucible, which consists of antimonic and sulphuric acids, may be converted, without loss, into pure antimoniate of antimony by calcination. If a great excess of free sulphur be intermixed with the precipitate to be oxidized, this is removed preliminarily by washing the dried filter with sulphuret of carbon, in accordance with the process to be described hereafter more completely. As precipitates of sulphuret of antimony, with or without free sulphur, readily take fire when fuming nitric acid is dropped upon them, it is advisable to moisten the mass with only 4 or 5 drops of acid of spec. grav. 1·42 before the addition of the fuming acid. The oxidation of sulphuret of antimony is effected somewhat more

conveniently than by this method by simple calcination with peroxide of mercury. If finely powdered sulphuret of antimony be heated with exactly the amount of peroxide of mercury which is necessary for its oxidation, a brisk detonation takes place, by which the mass is scattered about. But if thirty or fifty times the quantity of the oxidizing agent be employed, the combustion takes place quietly and without loss. For this purpose the mixture is slowly heated in an open porcelain crucible, and the temperature is moderated as soon as the oxidation commences; this point is recognized by the sudden evolution of gray mercurial fumes. When these have ceased, the temperature may be increased at pleasure, and the crucible may be left to itself, providing the lamp be previously so arranged that no reducing flame may be able to get into the crucible. To remove the last traces of oxide of mercury, which are combined with the antimonic acid, and are therefore obstinately retained, the crucible is heated for a time over the glass blowing lamp, until it no longer diminishes in weight. The antimoniate of antimony then remains as a delicate white powder, which does not in the least adhere to the walls of the crucible. However, oxide of mercury, even when prepared with the greatest care*, always leaves behind it after the volatilization a small residue which must be determined once for all and deducted from the found amount of antimoniate of antimony As this residue is rarely more than a few thousandths, the oxide of mercury employed in the oxidation need not be very accurately weighed. In a porcelain crucible the volatilization of the oxide of mercury takes place so slowly, that it is far more advisable to make use of a platinum crucible, previously lined with oxide of mercury in order to protect it from the action of the sulphuret of antimony. This lining, which renders it possible even to heat metallic antimony in a platinum crucible, is effected in the following way:—The closed end of a common test-tube is softened under the glass-blowing lamp, placed, whilst still soft, in the centre of the platinum crucible destined to the oxidation, and blown out into a small flask, which under these circumstances acquires exactly the form of the internal cavity of the crucible. By breaking away the bottom of this little flask and carefully fusing the sharp edge thus produced until it is smooth, a hollow mould, open above and below, is obtained, for which the cavity of the crucible forms an accurately fitted matrix. To effect the lining by the agency of this little instrument, it is forced into the crucible after this has been loosely filled up to the margin with dry oxide of mercury; the oxide which penetrates into the cavity of the mould being shaken out from time to time. The inner wall of the crucible is thus clothed with a layer of oxide of mercury of from $\frac{1}{2}$ to 1 line in thickness, which, after the removal of the mould, adheres with sufficient firmness to maintain its position for some time even when ignited. If the mass to be oxidized, intimately mixed with oxide of mercury, be placed in the crucible

* It is most easily prepared by precipitating a hot solution of bichloride of mercury with an *excess* of caustic potash. The yellow oxide thus obtained may be easily washed by decantation with boiling water.

thus prepared, the oxidation may be effected in one-third or one-fourth of the time required in a porcelain crucible, without the platinum being much acted upon.

If the sulphuret of antimony contain free sulphur intermixed with it, this must be removed, before the oxidation, by means of sulphuret of carbon, because, even when a great excess of oxide of mercury is present, it gives rise to a slight detonation, which would cause loss. This washing with sulphuret of carbon is most simply effected in the following way:—The funnel containing the filter with the thoroughly dried sulphuret of antimony mixed with sulphur, is placed upon a common test-glass, and from 10 to 12 grms. of sulphuret of carbon are poured upon the precipitate from the margin. The fluid, which runs through in two or three seconds, is poured back upon the filter 8 or 10 times, the funnel being placed alternately upon two test-glasses. To enable the same sulphuret of carbon to be used in repeating the same operation four or five times, it is distilled through a conducting tube fastened upon the test-glass into another test-glass surrounded by cold water, by immersing the glass containing the sulphuret of carbon in a beaker filled with hot water. After the completion of the distillation there remains a small drop of sulphur containing sulphuret of carbon, which solidifies when poured out. If the sulphur solidified from this drop be very small in amount, it is unnecessary to continue the extraction any further. With 10 to 15 grms. of sulphuret of carbon the precipitate may be sufficiently freed from sulphur in the course of a few minutes.

In the following experiments made to test the method, metallic antimony, reduced from antimoniate of soda and fused again with pure oxide of antimony, was employed. The first experiment was performed by myself, the second by Clessin, and the third by Jäger.

1. 43·59 centigrms. Sb gave 54·87 centigrms. Sb^2O^3.
2. 50·28 „ „ „ 63·76 „ „
3. 30·72 „ „ „ 38·88 „ „

If the calculation be based upon the equivalent of antimony (1529·2) established by Dr. Dexter's admirable investigations, we get,—

1. for 43·59 centigrms. Sb employed 43·49 Sb.
2. „ 50·28 „ „ „ 50·54 „
3. „ 30·72 „ „ „ 30·82 „

In an experiment (1) made by myself, and another (2) by Heydenreich, in which a native sulphuret of antimony containing only sulphur and antimony was employed,—

1. 0·2354 grm.* SbS^3 gave 0·2132 grm. Sb^2O^3.
2. *a.* 0·3670 „ † „ „ 0·3313 „ „
   b. 0·1993 „ „ „ 0·4143 „ $BaO\,SO^3$.

* Oxidized by oxide of mercury. † Oxidized by nitric acid.

If in the first experiment we calculate the sulphur from the loss, these experiments give—

	Calculated.	Found.	
		Exp. 1.	Exp. 2.
Antimony	71·82	71·79	71·56
Sulphur.....	28·18	28·21	28·52

For the separation of arsenic from antimony, we may avail ourselves of a peculiar behaviour exhibited by the sulphurets of these metals towards bisulphite of potash. Thus, if freshly-precipitated sulphuret of arsenic be digested with sulphurous acid and the above-mentioned salt, the precipitate is dissolved. If the heat be raised to the boiling-point, the fluid becomes turbid from the separation of sulphur, which disappears again for the most part by long boiling. After the expulsion of the sulphurous acid, the fluid contains arsenite and dithionite of potash. Leaving out of consideration the secondary reactions which occur at the same time, this decomposition takes place in accordance with the following equation,—

$$2As S^3 + 8(KO, 2SO^2) = 2(KO, AsO^3) + 6(KO, S^2 O^2) + 3S + 7SO^2.$$

Sulphuret of antimony and sulphuret of tin do not exhibit this reaction. Both of them therefore may be most simply separated from sulphuret of arsenic, by precipitating their solution in sulphuret of potassium by a great excess of an aqueous solution of bisulphite of potash, digesting the fluid on the water-bath for some time with the precipitate, and then boiling it until about two-thirds of the water and all the sulphurous acid are driven off. The sulphuret of antimony left is free from arsenic, whilst the filtered fluid contains all the arsenic as arsenious acid, and may be precipitated directly by sulphuretted hydrogen. Some examples will best illustrate the method of separation founded upon this reaction. For this purpose I select first of all an analysis of an impure commercial antimony, made by Heydenreich.

1. 0·2315 grm. of the metal, pulverized as finely as possible, were weighed in a platinum crucible capable of containing only about 20 grms. of water, treated with a concentrated solution of monosulphuret of potassium, and digested in the water-bath with the addition of a little sulphur until all the antimony was dissolved. The separated basic metallic sulphuret (A.) was collected upon a filter only 1·5 centimetre in depth, after the fluid had been diluted with a little water. The fluid filtered into a flask capable of containing 1 litre, when precipitated by a solution of sulphurous acid, digested and evaporated to $\frac{1}{3}$rd of its original volume, and until all the sulphurous acid was driven off, gave a precipitate of sulphuret of antimony, which was collected, after the lapse of 24 hours, in a weighed filter, and after washing, drying, and treatment with sulphuret of carbon, weighed 0·3502 grm. 0·1659 grm. of this, calcined with 15·27 grms. of oxide of mercury, gave 0·1440 grm. $Sb^2 O^3$. As 1 grm. of this oxide of mercury left a residue of 0·00045 grm. when volatilized, 0·1440 grm. represented 0·1372 grm. of pure antimoniate of antimony after the deduction of this residue.

2. From the fluid freed from antimony all the arsenic was thrown down as sulphuret of arsenic by a single passage of sulphuretted hydrogen. The precipitate, separated by filtration, oxidized, and treated with solution of chloride of magnesium and ammonium containing ammonia, gave 0·0055 grm. $\left.\begin{matrix}Mg^2O\\NH^4O\end{matrix}\right\}AsO^5+HO$. When, as in the present case, small quantities of sulphuret of arsenic which are mixed with much sulphur are to be determined, chlorate of potash and muriatic acid, or nitric acid of spec. grav. 1·42, must not be employed for the oxidation of the sulphuret of arsenic. In the former case a loss in chloride of arsenic is unavoidable; in the latter the temperature of the oxidizing fluid rises above 233° F. and causes the fusion of the sulphur into drops, which may easily envelope traces of sulphuret of arsenic and protect them from the action of the acid. For the oxidation of sulphuret of arsenic, therefore, it is far more advisable to employ fuming nitric acid, as its boiling-point is below the melting-point of sulphur. To avoid the formation of a hydrated acid with a higher boiling-point, it is the best plan to oxidize the arsenical precipitate and its filter, both thoroughly dried, by themselves, by dropping a considerable excess of fuming nitric acid upon the substances placed in a porcelain cup with a cover, and after the most violent reaction has ceased, heating the fluid in the water-bath until all the sulphur has disappeared and the nitric acid is evaporated to a small volume. This process, by which the sulphur is oxidized in the shortest time, also possesses the advantage, that if, during the filtration of the sulphuret of antimony, *small* quantities of the precipitate have passed through the filter, these remain as antimonic acid during the oxidation of the sulphuret of arsenic and may afterwards be determined. When any traces of antimonic acid have been separated by filtration, the solution in nitric acid is *gently* heated and mixed with a little chlorate of potash, in order to effect the still more complete oxidation of the substances formed from the paper, which may otherwise be easily precipitated by ammonia.

3. From the burnt filter containing the basic metallic sulphurets (A.), the following substances were obtained by the known methods:—

Peroxide of copper	0·0011 grm.
Peroxide of iron	0·0009 „
Sulphate of lead	0·0005 „

The impure antimony examined consequently contains,—

Antimony	99·172
Arsenic	0·938
Copper	0·004
Iron	0·003
Lead	0·002

In an analysis of another commercial antimony made in the same way by Kienscherf, the following results were obtained:—

0·7640 grm. of the metal furnished 0·004 of arseniate of ammonia and magnesia dried at 212° F., and 1·1216 grm. of sulphuret of antimony treated with sulphuret of carbon, of which 0·2225 grm. gave 0·1184 grm. Sb^2O^3, when calcined with oxide of mercury. The basic metallic sulphurets which remained when the antimony was dissolved in sulphuret of potassium furnished 0·0081 of sulphate of lead and 0·0023 of oxide of copper. These experiments lead to the following composition:—

Antimony	98·53
Arsenic	0·21
Copper.....	0·24
Lead	0·72

In another analysis made by Diffené of a mixture of 0·4322 grm. of arsenious acid with 0·3150 grm. of the native, chemically pure sulphuret of antimony used in the above analyses, there were obtained 0·4196 grm. of sulphuret of antimony, of which 0·2062 grm. gave 0·1392 grm. Sb^2O^3, and 1·2650 grm. of sulphuret of arsenic containing sulphur, which furnished 0·821 grm. $\left.\begin{matrix}Mg^2O\\NH^4O\end{matrix}\right\}AsO^5+HO$. This gives—

	Employed.	Found.
Sulphuret of antimony	42·16	41·84
Arsenious acid	57·84	57·74

I give one other analysis made by F. Goppelsröder, in which a cobalt-glance free from antimony, mixed with a weighed quantity of the above mentioned pure native sulphuret of antimony, was employed. This mixture consisted of 0·254 grm. of sulphuret of antimony and 0·5476 grm. of crystallized cobalt-glance. It was digested at 212° F. with solution of sulphuret of potassium in a small platinum crucible, until the greater part of the sulphuret of arsenic and sulphuret of antimony was extracted. The remaining basic metallic sulphurets were collected, in order to separate the last traces of acid sulphur compounds contained in them, upon a small filter, only 2 or 3 centimetres in depth, washed, and oxidized with nitric acid; the oxides formed were again treated with some sulphur and the solution of sulphuret of potassium in the platinum crucible, and this second solution was added to the first. The analysis effected as above, gave 0·2800 grm. of sulphuret of antimony, of which 0·234 grm. furnished 0·1921 grm. Sb^2O^3 when calcined with oxide of mercury; 0·6080 grm. of arseniate of ammonia and magnesia dried at 212° F.; 0·1902 grm. of protoperoxide of cobalt; 0·0623 grm. of peroxide of iron; and 0·0324 grm. of sulphate of lead.

To determine the sulphur, 0·8885 grm. of the cobalt-glance employed in the formation of the mixture were oxidized by fuming nitric acid until the sulphur was completely dissolved. The solution gave 1·1653 grm. of sulphate of baryta. From these experiments we get the following composition:—

	Employed.	Found.		Found.	Calculated from the formula (Co As Co S^2).
Sulphuret of antimony	31·69	31·88	As	29·99	29·80
			S	12·29	12·72
Cobalt-glance	68·31	67·91	Co	17·43	17·06
			Fe	5·44	5·32
			Pb	2·76	2·70

As bisulphuret of tin is not dissolved by long boiling with sulphurous acid and bisulphite of potash, it may be separated from arsenic in the same way as antimony. For this purpose the process is exactly the same as for the separation of the latter metal, except that in the washing of the sulphuret of tin, particular precautions must be observed. Thus, if bisulphuret of tin be washed with pure water, the fluid passing through the filter is always turbid and stops up the pores. This inconvenience is avoided by a method, which also does most excellent service in other cases. This consists simply in washing the precipitate completely with a concentrated solution of chloride of sodium, and then removing the latter by washing with a solution of acetate of ammonia, which must contain a slight excess of acetic acid. The same object would indeed be attained by using the latter fluid alone without any employment of a solution of chloride of sodium; but arsenious acid cannot be thrown down completely by sulphuretted hydrogen from the neutral or even from the acid solution of acetate of ammonia, as the salt is partially decomposed by sulphuretted hydrogen into free acetic acid and sulphuret of ammonium, which again dissolves the precipitated sulphuret of arsenic. The washing-water running off when the solution of chloride of sodium is washed out must therefore never be added to the fluid of the analysis. The acetate of ammonia remaining with the washing-water in the precipitate evaporates during the desiccation of the filter, and leaves the sulphuret of tin in a pure state; this is converted into stannic acid by ignition in contact with the air, and weighed in that form.

To test the method, a mixture of 0·1981 grm. of arsenious acid with 0·8710 grm. of tinfoil was digested with solution of potash after the addition of sulphur in a platinum crucible on the water-bath until the tin was dissolved, leaving a little sulphuret of lead. The latter, treated with nitric and sulphuric acid, gave 0·0030 grm. of sulphate of lead. By further treating the solution with sulphurous acid, there were obtained 0·2356 grm. of stannic acid and 0·3779 grm. $\left.\begin{matrix}Mg^2O\\NH^4O\end{matrix}\right\}AsO^5+HO$. From these data the following composition is deduced:—

Arsenious acid	51·43	51·26
Tin	48·05	48·22
Lead	0·52	0·52

Liebig's *Annalen*, April 1858, p. 1.

Processes for the Preparation and Analysis of Oxide of Uranium. *By* L. KESSLER.

The processes recommended for the separation of uranium from the metals which accompany it in minerals, all leave something to be desired. That of Arfvedson, which is the best and most adopted, leaves the oxide of uranium contaminated with oxides of nickel and zinc. The further treatment of the protoxide does not easily effect their complete elimination. On the other hand, although the crystallization of the double sulphates of uranium and potassium or sodium allows the preparation of perfectly pure oxide of uranium, this method is not analytical. The author's process is founded on the great affinity of the alkaline bicarbonates for oxide of uranium, and on the small affinity of uranium for sulphur.

Pitchblende is dissolved in nitric acid, water is added, and a precipitate is produced by sulphuretted hydrogen at the temperature of about 86° F., to separate arsenic, copper, and lead. The iron in the liquid is then again oxidized either by chlorine or by hot nitric acid. Tartaric acid is added, the fluid is saturated with ammonia, when everything remains in solution. Bicarbonate of soda well saturated with carbonic acid is then added; then submitting it rapidly again to the action of sulphuretted hydrogen, as long as a precipitate is formed, sulphurets of zinc, iron, nickel, and sometimes cobalt are separated, whilst the oxide of uranium remains in solution. These precipitates are washed with a dilute solution of bicarbonate of soda saturated with carbonic acid, and containing sulphuretted hydrogen.

For analysis, bicarbonate of ammonia would probably produce the same effect as that of soda, and furnish an oxide of uranium free from alkali.

During the passage of the sulphuretted hydrogen through the tartaric acid fluid, care must be taken to maintain an excess of carbonic acid, which is liable to be displaced by SH^2, and which prevents the oxide of uranium from becoming converted into sulphuret and the other metallic sulphurets from forming green sulphosalts and passing through the filter. This is easily done by adding some fragments of marble to the sulphuret of iron employed in furnishing the sulphuretted hydrogen.—*Comptes Rendus*, March 15, 1858, p. 530.

On the Preparation of Chromate of Lead, for Use in Elementary Analyses. *By* Dr. H. VOHL.

The employment of chromate of lead in elementary analyses, in which it has many advantages over peroxide of copper, is considerably limited, partly by its cost, and partly by its troublesome preparation; moreover, it could not hitherto be restored to its original condition like oxide of copper which has been used, so that after it had served twice or at the utmost three times, it became completely useless. The behaviour of the nitrates to oxide of chro-

mium at a red heat, led the author to examine into the action of nitrate of lead upon oxide of chromium. He mixed together 1 equivalent of each substance in fine powder, and heated the mixture in a porcelain crucible over the spirit-lamp. A considerable reaction very soon took place. The mass caked together, and a great quantity of nitrous acid was evolved. When the evolution of gas had ceased and the mass was more strongly heated, it fused, and on cooling furnished a radiately crystalline body of a dark reddish-brown colour, which, when triturated, gave a brownish-yellow powder, and proved to be pure chromate of lead. When this salt is employed in elementary analyses, it is principally only the chromic acid that is deprived of its oxygen; and used chromate of lead may be again converted into the pure salt by moistening it with nitric acid and afterwards calcining it.—Liebig's *Annalen*, April 1858, p. 127.

On some Reactions of the Salts of Lime and Magnesia.
By T. Sterry Hunt*.

In a recent paper on the earthy carbonates†, Bineau concludes that the carbonates of magnesia react with the soluble salts of lime like the corresponding carbonates of the alkalies. This is so far true that a solution of bicarbonate of magnesia precipitates carbonate of lime from a solution of chloride of calcium, while the basic carbonate of magnesia separates the carbonate of lime from its solution in carbonic acid. It results from this that when bicarbonate of soda is added to mixed and somewhat dilute solutions of chlorides of calcium and magnesium, the whole of the lime is precipitated as a nearly pure carbonate, while the magnesia remains dissolved either as chloride, or as bicarbonate, which is much more soluble than stated by Bischof, since according to the determinations of Bineau and my own, water may dissolve as bicarbonate more than 1 per cent. of MgO.

I have found that when we evaporate, at from 60° to 100° F., a solution of bicarbonate of lime with an excess of sulphate of magnesia, the whole of the lime is separated in the form of gypsum, and there remains bicarbonate of magnesia in solution. The same thing happens in presence of sea-salt and chloride of magnesium, provided sulphates are present. These solutions of bicarbonate of magnesia give rise to deposits of carbonate of magnesia by further evaporation. Deville has observed that the slow action in the presence of water, between carbonate of magnesia and bicarbonate of soda, aided by a gentle heat, results in the production of a crystalline anhydrous double carbonate of magnesia and soda, analogous to dolomite; and I am led from some yet unfinished experiments to suppose that a similar reaction between the carbonates of lime and magnesia in the presence of carbonic acid may yield the double carbonate of lime and magnesia, and thus explain the formation of magnesian limestone.—Silliman's *American Journal for July* 1858.

* Extract of a letter to J. D. Dana, dated Quebec, May 29, 1858.

† Ann. de Chimie et de Physique, sér. III. vol. li. p. 302.

THE CHEMICAL GAZETTE.

No. CCCLXXXI.—September 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Potash upon Pelosine.

By C. GREVILLE WILLIAMS*.

IN my investigation on chinoline and its homologues, I have shown that the reactions of some bases differ with the sources from whence they are procured. Thus chinoline from coal-tar (however pure it may be) refuses to give the characteristic crystalline bichromate which is yielded so readily by the same base when procured from cinchonine. This fact made me desirous of comparing as many specimens as possible derived from different sources. The desire became increased on finding that the chinoline from cinchonine was capable of affording a superb and fast blue dye by processes which, applied to an equally pure coal-base, yielded no reaction.

Owing to a too great reliance on odour, errors have more than once crept into this branch of organic chemistry. Chinoline has, consequently, often been stated to be produced in reactions which in fact do not yield a trace. One of the processes said to afford it is the distillation of the chromate of pelosine†. The violent combustion I observed to take place on heating the bichromate of chinoline, led me to have strong doubts of the correctness of M. Bödeker's statement; I therefore felt desirous of ascertaining the nature of the reaction taking place on distilling pelosine itself with alkalies, this being a process far more likely to yield chinoline than the method previously described.

When the medicinal extract of *Pareira brava* is digested with cold water, the insolubility of pelosine causes the greater portion to remain behind in the crude state, under the form of a pale brown granular powder. For a small specimen of this substance I am indebted to my friend Mr. George Whipple.

On distilling pelosine in an iron alembic with a concentrated solution of potash, great frothing ensued, and extreme care was requisite to prevent the contents of the retort from passing into the receiver. The distillate had a most powerful and persistent odour of boiled shrimps. As soon as the greater part of the water was

* Communicated by the Author.

† Bödeker, Ann. der Chem. und Pharm., lxix. 53.

expelled, and the potash entered into fusion, the distillate became milky, and, at this point, a splinter of deal wood wetted with hydrochloric acid and introduced into the tubulature of the alembic, instantly acquired a brilliant crimson colour from the presence of pyrrol. Towards the end of the distillation torrents of gas were given off, which on ignition burned with a brilliant flame. On saturating the bases with hydrochloric acid, and heating the fluid, it turned nearly black, owing to the separation of the peculiar substance always resulting from the decomposition of pyrrol by acids. The entire fluid was evaporated to dryness, and the soluble chlorides dissolved out with alcohol. The alcoholic fluid left on evaporation a highly coloured mass, which was dissolved in water and the colouring matter removed by the addition of a few drops of solution of bichloride of platinum, by which it was instantly precipitated, the fluid on filtration becoming nearly colourless. An excess of a concentrated solution of bichloride of platinum was then poured in, and the whole left to repose for some hours. At the end of this time the fluid had become almost filled with brilliant crystals reflecting prismatic colours. This formed Crop I. The mother-liquid was left for a night *in vacuo* over sulphuric acid. In the morning a number of deep red crystals arranged in rosettes had formed (Crop II.). By proceeding in this manner seven crops of crystals were obtained. The sixth and seventh were in such small quantity that it was necessary to mix them in order to obtain sufficient to enable a platinum determination to be made.

I.	·2326 grm. of crop		I.	gave on ignition	·0954 platinum.
II.	·2158	„ „	II.	„ „	·0900 „
III.	·2018	„ „	III.	„ „	·0842 „

or, per cent.,—

I.	II.	III.	Mean.	Theory $C^2H^6N, HCl, PtCl^2$.
41·01	41·71	41·72	41·48	41·68

It is evident from these numbers that the base was methylamine.

Rejecting the fourth crop, to which an accident happened, we have for the fifth and sixth crops:—

V.	·2024 grm. of crop		V.	gave on ignition	·0800 platinum.
VI.	·1942	„ „	VI. and VII.	„	·0772 „

Reducing these numbers to per-centages, we have—

V.	VI.	Mean.	Theory $C^4H^7N, HCl, PtCl^2$.
39·53	39·75	39·64	39·36

The above numbers correspond exactly with bimethylamine. It is evident that they will do equally well for ethylamine. The probabilities are, however, in favour of the base first mentioned. The quantity present was, of course, far too small to permit any experiments to be made with a view of deciding this question.

Although most of the vegetable alkaloids yield volatile bases on

distillation with the fixed alkalies, the decomposition is never capable of being represented by an equation accounting for all the products. As we are still ignorant of the molecular constitution of the natural bases, so we are unable to predict the nature of those resulting from their metamorphosis under the influence of heat or powerful reagents. There are, however, two substances which I have always found to be produced by the action of heat upon them, namely pyrrol and ammonia. This fact loses none of its significance from the circumstance that almost all the organic matters containing carbon and nitrogen, which I have examined, do the same. It is probable that most of the natural bases treated with alkalies at a temperature insufficient to char them, would undergo a more definite decomposition. This is rendered the more likely from the results of MM. von Babo and Keller's experiments* on the action of alcoholic potash on piperine. In that reaction piperidine and piperic acid appear to be the only products formed.

It is true that, as yet, the study of the action of the fixed alkalies on the natural alkaloids has not resulted in a knowledge of their constitution, yet the information obtained has been of a very suggestive character, and it becomes desirable to accumulate as many facts as possible, previous to making such generalizations as may enable us more clearly to comprehend the manner in which the bodies under consideration break up. The following list contains what is known with regard to the basic products of the action of the fixed alkalies on the natural alkaloids:—

Caffeine.	Methylamine.
Cinchonine.	Pyridine, picoline, lutidine, collidine, chinoline, lepidine, pyrrol.
Codeine.	Methylamine, trimethylamine, or propylamine.
Morphia.	Methylamine.
Narcotine.	Trimethylamine or propylamine, pyrrol, and probably other bases.
Papaverine.	Bimethylamine or ethylamine, trimethylamine or propylamine.
Pelosine.	Methylamine, bimethylamine or ethylamine, pyrrol.
Piperine.	Piperidine, and a base or bases unknown.
Quinine.	Probably the same as cinchonine.
Strychnine.	Probably the same as cinchonine.

The alcohol bases have been produced in a vast number of reactions like the above; but although the amount required to enable the action of the iodides of the alcohol radicals to be tried is far from large, still they are seldom procured in sufficient quantity for the purpose. The result is that great uncertainty prevails as to their true nature.

It is curious that it has been assigned† as a reason for the base of the formula $C^6 H^9 N$ found in the flowers of the white thorn and other varieties of *Cratægus*, being the true propylamine, that they

* Chem. Gaz., July 1, 1858.

† Gmelin's Handbook of Chemistry, vol. ix. p. 413 (Cavendish Soc. Translat.).

(the flowers) have no fishy odour. But I have observed (long before I was aware of the fact of there being a base present) that the blossoms of the *Cratægus oxyacantha* have, at times, a distinctly fishy odour; marked, it is true, by the well-known perfume of the plant, but still perfectly obvious to most persons if smelling at a considerable mass of the flowers.

On some Compounds of Chromic Acid with Oxide of Mercury.
By Dr. A. Geuther.

The supposition that in the compound $KCy^2, HgCy + HgO, CrO^3$, there existed a neutral chromate of mercury, furnished the inducement to the following experiments, which have shown the mode of preparation of the neutral chromate of mercury by itself, and also that of a new basic salt.

Neutral Chromate of Mercury=HgO, CrO^3, is produced when nearly equal parts of pure dry chromic acid dissolved in water and yellow oxide of mercury are boiled together and slowly evaporated until all the oxide has disappeared and been replaced by red crystals. Notwithstanding the constant movement of the fluid, these crystals acquire a considerable size and are finely developed. After refrigeration the mother-liquor is poured away, and the crystals are placed on bibulous paper, by which the last traces of adherent fluid are removed. The mother-liquor, when further concentrated, furnishes new portions of the compound.

The crystals are rhombic prisms of a deep garnet-red colour, which is rendered somewhat darker by heat, and is then nearly the same as that of dry chromic acid. The analysis was effected by the ignition of the dry compound; it is decomposed into mercury, which is driven off, and oxide of chrome, which remains. 0·6133 grm. of the dried salt left on ignition 0·1495 Cr^2O^3=0·1958 CrO^3, which gives:—

	Calculated.	Found.
HgO	68·06	..
CrO^3	31·94	31·91

The crystals are decomposed by water even in the cold, but completely when heated, forming the amorphous compound $3HgO, CrO^3$ and 2 atoms of free chromic acid. Crystals which had been treated with cold water contained 30·26 and 27·3 per cent. of chromic acid, but after boiling only 13·93 per cent. CrO^3; the formula $3HgO, CrO^3$ requires 13·53 per cent. The crystals dissolve readily and completely in muriatic acid; from this solution soda throws down yellow oxide of mercury. Cold concentrated nitric acid converts it into an amorphous yellow compound, a considerable portion of which is dissolved*; moderately concentrated nitric acid and sulphuric acid have the same action, except that a larger quantity of

* If this solution be poured into a large quantity of water, a precipitate is thrown down which is at first yellow, but afterwards becomes of a beautiful cochineal-red; it contains 13·34 per cent. CrO^3, and is therefore $3HgO, CrO^3$. Its unusually dark colour is probably due to crystalline structure.

the yellow compound remains undissolved. The latter, like the yellow compound produced by the action of solution of soda upon the crystals, appears to be identical with the compound $7HgO, 2CrO^3$, shortly to be described.

If the very dilute mother-liquor which remains after the first crystallization of the preceding compound be mixed with solution of carbonate of soda until a precipitate is produced, and this be continued as long as the fluid remains slightly acid, a mixture of compounds is obtained. The first portion of the precipitate is rich in the compound $3HgO, CrO^3$, together with one containing more chromic acid. It is of a darker red colour and contains 16·4 per cent. CrO^3. The following portions which are thrown down whilst the solution is still strongly acid, consist principally of the above-mentioned compound, containing much chromic acid; they gave 20·8 per cent. CrO^3, the formula $2HgO, CrO^3$ requiring 19·0 per cent.; their colour, is lighter than that of the portions first precipitated, and rather a pretty orange. The last portions, up to the neutralization of the fluid, gradually become browner and contain considerable quantities of brown oxide of chrome $=Cr^2O^3, CrO^3$, for when treated with solution of soda and afterwards with nitric acid, a green solution is formed. In the last precipitate, therefore, the amount of chrome increases; such a brown portion contains 23·6 per cent. CrO^3. The origin of the oxide of chrome must be sought for in the chromic acid employed, which, when prepared from fluoride of chromium, must always be heated considerably to expel the hydrofluoric acid; during this a partial reduction and formation of Cr^2O^3, CrO^3 may have taken place.

We might be inclined to attribute the increased amount of chrome in the middle portions (20·8 per cent. CrO^3) to a smaller intermixture of oxide of chrome, which may increase and become predominant in the last portions; but they exhibit a different behaviour from the compound $3HgO, CrO^3$, which would have to be assumed in them, mixed with brown oxide of chrome. Thus, if they be boiled with dilute solution of soda, chromate of soda and oxide of mercury are not produced, as should then be the case, but they furnish chromate of soda and a yellow basic chromate of mercury, which is insoluble in moderately concentrated nitric acid. For this reason the author assumes that in the precipitate first obtained the compound $2HgO, CrO^3$ is mixed with $3HgO, CrO$, which is thrown down pure in the middle portions, and regards it as a double compound of $3HgO, CrO^3 + HgO, CrO^3 = 2(2HgO, CrO^3)$. It is soluble in muriatic and nitric acids, but is decomposed by boiling with solution of soda into neutral chromate of soda and the following compound.

Basic Chromate of Mercury of the formula $7HgO, 2CrO^3$, is obtained from the precipitate produced by carbonate of soda in the very dilute mother-liquor poured from the crystals of the neutral chromate, when this is boiled with solution of soda. It is best to exclude the last portions abounding in oxide of chrome entirely, and for this reason only to add carbonate of soda as long as the

precipitate is of a pure yellow colour, which is the case while the fluid has still a pretty strong acid reaction. The precipitate is washed immediately by decantation. After treatment with solution of soda it is treated with moderately concentrated nitric acid (in which it is nearly insoluble even when boiled), in order to purify it from oxide of mercury and any oxide of chrome. Its production is expressed by the equation $2(3HgO, CrO^3 + HgO, CrO^3) + 2NaO = 7HgO, 2CrO^3 + HgO + 2(NaO, CrO^3)$. It may also be regarded as consisting of 2 atoms of tribasic chromate of mercury and 1 atom of oxide of mercury $= HgO + 2(3HgO, CrO^3)$. It forms an amorphous, heavy, yellow powder with an orange tinge, which dissolves rapidly when heated in concentrated nitric acid only when it is freshly precipitated and has not been *boiled* (in solution of soda). It is converted into white sulphate of mercury only by concentrated sulphuric acid, and then only when heated, but muriatic acid readily takes it up. Analysis, by ignition, gave—

	Calculated.	Found.	
$7HgO$	88·19	..	..
$2CrO^3$	11·81	11·90	11·87

The same compound may also be obtained in other ways. If freshly precipitated yellow oxide of mercury be boiled with a concentrated solution of bichromate of potash for a long time, the former is converted into a tile-red powder with reception of chromic acid and formation of neutral chromate of potash; this powder so obstinately retains chromate of potash that it cannot be freed therefrom even by long washing. If an attempt be made to get rid of it by boiling, separate yellow particles become perceptible again in the powder, and the quantity of these increases the longer the boiling is continued. This red powder does not appear to be a constant compound, for analyses of different preparations gave dissimilar results. In one case the amount of chromic acid was 11·7 per cent.; in another 12·6 per cent. It appears consequently to be a mixture of $3HgO, CrO^3$ and $7HgO, 2CrO^3$, as the amount of chromic acid in the former is 13·5 and in the latter 11·8 per cent. When this body is freed by repeated decantations from the principal portion of the excess of chromate of potash and then heated with moderately concentrated nitric acid, partial solution takes place, whilst the yellow compound remains of the same appearance and with the same properties as that prepared by the method above described. Analysis confirms the identity of the two bodies; it gave—

	Calculated.	Found.
$7HgO$	88·19	..
$2CrO^3$	11·81	11·83

Liebig's *Annalen*, May 1858, p. 244.

On a new Ferrocyanide of Potassium and Copper. *By* P. Bolley.

In a coppering fluid composed of sulphate of copper (containing some iron) and solution of cyanide of potassium, I found, after it

had been standing for months imperfectly closed, a considerable quantity in proportion to the fluid of well-developed, brownish-red crystals deposited at the bottom. There were some which were about 2 lines in diameter. They were octahedra, very probably regular, but the determination of the system to which they belong could not be accurately effected from the surfaces not being perfectly smooth. The crystals had the greatest similarity with those of sulphate of chrome and alumina. My qualitative analysis furnished iron, copper, potassium, cyanogen, and water. The determination of the individual constituents, which was effected partly by myself and partly by my assistant, Dr. F. Moldenhauer, furnished the following average numbers:—

Potassium, average of	2	determinations		21·03
Copper	„	„	3	„ „ 22·64
Iron	„	„	3	„ „ 10·11
Nitrogen	„	„	2	„ „ 17·41
Carbon	„			15·57
The deficiency, considered as water				13·24

The carbon was determined by an elementary analysis and the nitrogen by soda-lime. The amount of cyanogen calculated from the nitrogen is 32·51, and from the carbon 32·9 per cent.; the average would therefore amount to 32·6 per cent.

					Found.
3 equivs.	Potassium	represent	117·6	=21·22	21·03
4 „	Copper	„	126·7	22·86	22·64
2 „	Iron	„	56	10·10	10·11
7 „	Cyanogen	„	182	32·83	32·60
8 „	Water	„	72	12·99	13·62

and the formula of the compound would be $3KCy, 2Cu^2Cy, 2FeCy + 8HO$, but it is more probable that the amount of water is only 7 equivs., corresponding with the cyanogen. I recommended Dr. Moldenhauer to make experiments upon the preparation of this salt; by boiling protocyanide of copper, Cu^2Cy, with ferrocyanide of potassium, filtering the solution, and leaving it to cool, he succeeded in obtaining a chocolate-brown powder, the identity of which with the above salt was proved by the determination of the copper, iron, and potassium.

Potassium.....	20·44 per cent.
Copper.....	24·33 „
Iron	10·48 „

Liebig's *Annalen*, May 1858, p. 228.

Note on two New Derivatives of Quinine and Cinchonine. *By* P. Schutzenberger.

When nascent hydrogen is set free by a mixture of zinc and sulphuric acid in the midst of a solution of sulphate of quinine, and the liquid is precipitated by an excess of ammonia after the lapse of some time, there remains, after the solution of the oxide of zinc, a

viscous, sticky body. This matter being dissolved in alcohol, filtered, to get rid of any small quantities of oxide of zinc, and then evaporated, left a transparent, somewhat resinous, and slightly greenish residue, possessing basic properties. This base, dried at 248° F., gave on analysis—

	Found.	Calculated.
C	66·2	66·66
H	7·9	7·77

which leads to the formula of a hydrate of quinine,

$$C^{40}\,H^{24}\,N^{2}\,O^{4},\,4HO.$$

The substance dried at 248° F., loses more water very slowly at 284° F. When dried at this temperature, it gave on analysis—

	Found.	Calculated.
C	68·40	68·37
H	7·53	7·06

leading to the formula

$$C^{40}\,H^{24}\,N^{2}\,O^{4},\,3HO,$$

or that of a hydrate of quinine with 3 equivs. of water.

At a temperature of 302° F. the product loses still more, and the formula obtained is that of a hydrate,

$$C^{40}\,H^{24}\,N^{2}\,O^{4},\,2HO,$$

which is stable and enters as such into combination with acids; thus, 0·366 gr. of the chloroplatinate of this base, dried at 212° F., and losing nothing at a higher temperature, gave,

Platinum..... 26·2 per cent.,

agreeing exactly with the formula

$$C^{40}\,H^{24}\,N^{2}\,O^{4},\,2HO,\,2(ClH,\,Cl^{2}\,Pt).$$

A second analysis gave exactly the same result.

Hydrate of quinine is uncrystallizable, resinous, soft at 95° F., and melts at 212° F. It is almost as bitter as quinine, gives a green colour, like it, with chlorine and ammonia, and is soluble in æther and alcohol. Its salts are more soluble than those of quinine. The sulphate crystallizes with difficulty.

Under the same circumstances cinchonine also furnishes a resinous, uncrystallizable hydrate, without any bitterness, very soluble in cold alcohol and æther, and furnishing very soluble salts. This hydrate contains 4 equivs. of water at 248° F.; of these it loses one at 284° F., and a second at 302° F., so that when dried at this temperature its formula is

$$C^{40}\,H^{24}\,N^{2}\,O^{2},\,2HO.$$

This is a stable hydrate which forms compounds with acids.

The analysis of the substance dried at 248° F. gave—

	Found.	Calculated.
C	69·46	69·76
H	8·02	8·10

Dried at 284° F. it gave—

	Found.	Calculated.
C	71·56	71·60
H	8·04	8·06

The chloroplatinate, dried at 212° F., and losing nothing at a higher temperature, gave 27·1 per cent. of platinum; the formula

$$C^{40}\,H^{24}\,N^{2}\,O^{2},\,2HO,\,2(ClH,\,Cl^{2}\,Pt)$$

requires 27·06 of platinum.

It is difficult to explain the fixation of water in the alkaloids by the agency of nascent hydrogen. From experiments still in progress, it appears that other alkaloids behave in the same way.

By the action of nitrous acid, the author has succeeded in preparing oxyquinine, oxynarcotine, oxybrucine, oxystrychnine, and oxycodeine.—*Comptes Rendus*, May 31, 1858, p. 1065.

Note on the Preparation of Calcium. By M. Liès Bodart.

The author and M. Gobin endeavoured to produce calcium by the action of sodium upon fused chloride of calcium at a high temperature, but all their attempts failed. They then replaced the chloride by iodide, when the reaction took place very distinctly, furnishing nearly the theoretical quantity of calcium.

The operation is effected in the following way:—Iodide of calcium is prepared by treating white marble with hydriodic acid; the fluid is rapidly evaporated and the residue fused without access of air. The iodide has the appearance of anhydrous chloride of magnesium. Equal equivalents of this and of sodium are put into an iron crucible; the crucible employed by the author is a cylinder of 15 centimetres in length and 3 centimetres in diameter, closed by a screw. It was put into the furnace, and the temperature was gradually raised to bright redness, without reaching a white heat; it was exposed to this temperature for an hour, and then taken out and left to cool.

On the surface of the substance there was an ingot of *three grammes* of calcium; the quantity of sodium employed was four grammes. The ingot was dull, covered with a very thin stratum of blackish substance, which is probably a suboxide of calcium. This is easily removed, when the metal is pale yellow, with a reddish reflexion. It decomposes water, and yet only burns in the air when heated to redness, when it throws off sparks in the manner of magnesium; the flame is yellow.

0·106 gr. were treated with water, when the metal completely disappeared without residue; a few drops of acetic acid were added to dissolve the lime, when oxalate of ammonia furnished an abundant precipitate which gave 0·353 gr. of sulphate of lime. 0·106 gr. of pure calcium should have given 0·360 gr. of sulphate of lime: the filtrate contained traces of iodide of sodium.—*Comptes Rendus*, July 5, 1858, p. 23.

Conversion of the Lactic Acid from Flesh into ordinary Lactic Acid. *By* A. STRECKER.

The author prepared the pure acid from carnilactate of zinc, which had exactly the composition ascribed to it by Liebig, ZnO, $C^6 H^5 O^5 + 2HO$, by decomposing the salt with sulphuretted hydrogen. The acid was evaporated to a syrup in the water-bath, and afterwards heated in the oil-bath to 265°—284° F. On cooling, the residue solidified into an amorphous mass, which had the character of anhydride of lactic acid. This mass, when boiled for some hours with an addition of oxide of zinc, dissolved, although slowly. The solution furnished by crystallization the zinc-salt of ordinary lactic acid, with all its properties (amount of water, found 18·1, calculated 18·2 per cent.). The lactic acid from flesh is consequently converted into ordinary lactic acid at a temperature of 266°—284° F.—Liebig's *Annalen*, cv. p. 313.

On the Decomposition of Piperine by Potash. *By* Prof. STRECKER.

The decomposition of oxygenated organic bases into volatile organic bases free from oxygen, and into other substances not volatile, is a reaction which, in spite of its great importance as giving a clue to the true constitution of the natural alkaloids, has been only imperfectly studied. The recent investigation of von Babo and Keller* of the decomposition of piperine into piperidine and a non-nitrogenous acid is an interesting example. But the explanation of the reaction offered by these chemists cannot be regarded as satisfactory; not so much that they leave undetermined the formula of the acid produced, which they say is either $C^{50} H^{34} O^{16}$ or $C^{50} H^{32} O^{16}$, as that the assumption of an acid containing 16 equivs. of oxygen, and yet partially volatile without decomposition, appears highly improbable. To explain the decomposition, it is also necessary to assume for piperine the formula $C^{70} H^{40} N^2 O^{12}$. This agrees but imperfectly with the analytical results of Regnault and Laurent, which correspond closely with the old formula $C^{34} H^{19} NO^6$.

From von Babo and Keller's analyses of piperic acid it is not easy to get at a better formula, and the author has accordingly prepared and analysed piperic acid and its silver-salt.

Piperic acid is readily obtained by boiling piperine with alcoholic potash: the potash-salt thus obtained was purified by repeated crystallization from water, decomposed by hydrochloric acid, and the piperic acid repeatedly crystallized from alcohol. On analysis it gave numbers leading to the formula

$C^{24} H^{10} O^8$.

	Calculated.		Found.		v. Babo and Keller.	
			I.	II.		
C^{24}	144	66·06	65·9	65·9	66·1	66·9
H^{10}	10	4·59	4·6	4·7	4·8	5·1
O^8	64	29·35				

* Chemical Gazette, January 1, 1858.

Piperate of silver was prepared by precipitating piperate of potash by nitrate of silver. The salt contained no water; it was dried at 212° F., and gave on analysis numbers closely agreeing with the formula

$$AgO, C^{24} H^9 O^7.$$

	Calculated.		Found.		
			I.	II.	III.
C^{24}	144	44·3	44·3	..	44·4
H^9	9	2·8	2·9	..	2·8
Ag	108	33·2	33·2	33·1	
O^8	64	19·7			

The analyses of von Babo and Keller also agree approximatively with the above formula.

These numbers may therefore fix the formula $C^{24} H^{10} O^8$, and in accordance therewith the decomposition of piperine into piperic acid and piperidine might be expressed by the equation

$$\underset{\text{Piperine.}}{C^{34} H^{19} NO^6} + 2HO = \underset{\text{Piperic acid.}}{C^{24} H^{10} O^8} + \underset{\text{Piperidine.}}{C^{10} H^{11} N}.$$

And the formula of piperine may probably be expressed by the scheme

$$N \begin{cases} C^{24} H^9 O^6 \\ C^{10} H^{10} \end{cases},$$

in which $C^{24} H^9 O^6$ expresses the monoatomic radical of piperic acid, and $C^{10} H^{10}$ the biatomic radical contained in piperine. And piperine would correspond to the amides prepared by Cahours, benzopiperidine, $\left.\begin{matrix} C^{14} H^9 O^2 \\ C^{10} H^{10} \end{matrix}\right\}$ N, and cumopiperidine, $\left.\begin{matrix} C^{20} H^{11} O^2 \\ C^{10} H^{10} \end{matrix}\right\}$ N.

Liebig's *Annalen*, March 1858.

On the Yellow Colouring Matter of the Fruit of Gardenia grandiflora. *By* F. Rochleder.

Lorenz Mayer has prepared and investigated the colouring matter of the Chinese yellow pods in Rochleder's laboratory. Rochleder states that the fruits were reduced to a coarse powder, and this was extracted with alcohol. The deep-coloured decoction was first strained through linen, then filtered through paper, and finally distilled in the water-bath. The aqueous residue is covered with a green or nearly black stratum, which is separated from the aqueous fluid by filtration through a moist filter. This mass possesses a rancid odour, and consists for the most part of a fluid fatty acid. Of a colourless crystallized body, which appears to be a mixture of two kinds of wax with very different melting-points, no quantity sufficient for investigation could be obtained.

The aqueous fluid, freed from fat, which remains after the alcohol is distilled off, was diluted with much water, and mixed with hydrate of alumina, prepared by the precipitation of alum, and thoroughly washed. After standing for several days, the fluid was separated by filtration from the alumina and the compounds of alumina formed.

The mass remaining on the filter is dingy, of a brownish yellow colour; it contains all the tannic acid, as well as some colouring substances produced by the decomposition of the colouring matter and tannic acid. The filtered fluid is mixed with an aqueous solution of basic acetate of lead, by which a fine orange precipitate is produced; this is rapidly filtered, washed with water upon the filter, then suspended in water and decomposed by a current of sulphuretted hydrogen, when the colouring matter is taken up and retained by the sulphuret of lead.

The sulphuret of lead is therefore thoroughly washed with water, and the filtered fluid and washing-water are set aside; the washed sulphuret of lead is then boiled with alcohol, which takes up the colouring matter, and the solution is separated from the sulphuret of lead by filtration upon a water-bath funnel. This solution is evaporated *in vacuo* over sulphuric acid, as the colouring matter would be altered by the continued application of heat. The amorphous residue is dissolved in water, of which the smallest possible quantity should be used; the solution is filtered from some separated sulphur, and again reduced to dryness *in vacuo* over sulphuric acid. Rochleder names this colouring matter

Crocine, because he finds it to be identical with that of the crocus; its composition is $2(C^{58}H^{42}O^{30})+HO$. When pounded it forms a bright red powder, which is readily soluble in water and alcohol. The solutions possess the colour of that of chromic acid. Lead-salts give orange-red precipitates with the colouring matter. The concentrated aqueous solution, when mixed with concentrated sulphuric acid, becomes first indigo-blue, then violet. The aqueous solution of crocine is decomposed by dilute sulphuric and muriatic acids when heated; a product of decomposition of a fine dark red colour is separated. The fluid retains a yellow colour from a small quantity of this product; it contains in solution a sweet crystallizable, colourless body. Analyses:—

	I.	II.	III.
C	54·87	54·78	54·76
H	6·71	6·55	6·93
O	38·42	38·67	38·31

In the decomposition of crocine by muriatic or sulphuric acid, a body is obtained to which the author gives the name of

Crocetine; its composition is $C^{42}H^{23}O^{11}$. It is a dark red, amorphous powder, sparingly soluble in water, readily soluble in alcohol, and not insoluble in æther. With concentrated sulphuric acid it exhibits the same blue colour as crocine. Lead-salts give citron-yellow precipitates with solutions of crocetine. Crocetine is a true dye-stuff; tissues mordanted with tin-salt are dyed dingy greenish yellow by it, but when treated with water containing ammonia acquire a brilliant golden-yellow colour, which resists exposure to light and air, and undergoes no alteration when washed with soap. The Chinese, as is well known, dye the yellow robes of the mandarins with the fruits of the *Gardenia*.

The decomposition of crocine by muriatic acid, as well as by sulphuric acid, takes place with remarkable facility. It is however indispensably necessary to effect this decomposition in an atmosphere of carbonic acid or hydrogen, as oxygen is taken up by hot solutions of crocine, and still more readily by those of crocetine. This alteration is perceptible even by the less pure colour of the crocetine which has been separated with access of air. That a body which is readily altered by the oxygen of the air, is still more rapidly attacked by it at the moment of separation, is no more than was to be expected. In fact, analyses of crocetine which had been prepared with access of air, furnished a far smaller amount of hydrogen than that of pure crocetine.

In the decomposition of a very concentrated solution of crocine by dilute acids, the greater part of the crocetine (about 41 per cent.) separates from the fluid, so that about 8 per cent. remain dissolved in the fluid, which receives a golden-yellow colour from it.

If the decomposition be effected by muriatic acid and the fluid filtered from the crocetine be treated according to the method formerly described by the author, there remains after evaporation a readily crystallizable body of a sweet taste.

In the attempt to determine the quantity of this sugar with Fehling's fluid, the following results were obtained:—In the decomposition with muriatic acid there were found 28·5 per cent., and in that with sulphuric acid 27·94 of sugar ($=C^{12}H^{12}O^{12}$). But as no third volatile or non-volatile product of decomposition could be discovered, this is not grape-sugar, but another hydrate of carbon which reduces exactly half as much peroxide of copper as grape-sugar. Analyses of crocetine:—

	I.	II.
C	64·33	64·60
H	7·52	7·26
O	28·15	28·14

This composition of the colouring matter does not allow us to overlook some interesting relations to other constituents of (the fruits of) *Gardenia florida*. Von Orth, who investigated these fruits four years ago, found a tannic acid in it which is retained by the alumina in the process recommended by L. Mayer for obtaining the yellow colouring matter. Its composition was found by von Orth to correspond with the formula $C^{46}H^{28}O^{26}$. If the elements of sugar be deducted from this substance, there remains a body of the formula $C^{34}H^{18}O^{16}$; that is to say, a substance which contains about 5 equivs. less hydrogen and 5 equivs. more oxygen than crocetine. A resinous colouring matter which was analysed by von Orth, gave numbers corresponding with the empirical formula $C^{30}H^{19}O^{21}$. This colouring matter must receive the formula $C^{28}H^{17}O^{11}$, which makes this resinous colouring matter appear to be the last member of the same series of homologous substances to which crocetine belongs, for $C^{28}H^{17}O^{11}$ differs by $C^{6}H^{6}$ from crocetine$=C^{34}H^{23}O^{11}$.

All the reactions of the colouring matter of the fruits of *Gardenia grandiflora*, as well as its properties, agree perfectly with those of polychroite or the colouring matter of saffron.

The composition of the latter colouring matter was ascertained by Quadrat. He found 54·54 and 54·47 per cent. of carbon, consequently rather too little (0·4 per cent.), and also too little hydrogen; he evidently operated upon an impure colouring matter.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxix. p. 1.

On the Nitrurets of Tungsten and Molybdenum. *By* Professor Wöhler.

If one of the chlorides of tungsten or molybdenum be placed in the closed end of a long glass tube, with dried fragments of muriate of ammonia above it, and the tube be heated to redness, first in the empty part, and afterwards at the end, so that the two salts may be volatilized and exposed to a red heat whilst mixed in a gaseous form, a complete mutual decomposition takes place, and after all excess of muriate of ammonia has been driven off, the entire inner wall of the tube is found coated with a speculum of a black, semi-metallic substance, which may be removed partly in brittle crusts, and partly in black powder. It has the same aspect with both metals, and it consists either of the nitruret of the metal, or of one of the amide compounds. When heated in the air it burns into tungstic or molybdic acid. When fused with hydrate of potash it forms a great quantity of ammonia.—Liebig's *Annalen*, February 1858, p. 258.

ANALYTICAL CHEMISTRY.

On the Detection of Uric Acid. *By* G. Städeler.

Solutions of uric acid are not precipitated by acetate of lead, but are completely precipitated by basic acetate of lead. If the fluid to be examined, which must be previously freed from albumen when this is present, be mixed with acetate of lead, filtered immediately from the precipitate formed, and then mixed with basic acetate of lead, the whole of the uric acid will be separated in the form of urate of lead in the course of 24 hours. The organs or entire animals (such as Insects, &c.) are triturated with pounded glass, treated with two or three times their volume of alcohol, and left standing for 12—18 hours. The fluid is then pressed out and filtered, and the whole residue, which contains all the uric acid, is uniformly diffused in water, and heated for an hour in the water-bath. The fluid is then separated by pressure, and the uric acid thrown down as above described. The urate of lead is finally suspended in water, and decomposed by sulphuretted hydrogen, when the fluid is heated to boiling and filtered. On evaporating the colourless filtrate the uric acid separates in colourless or slightly brownish crystals, sometimes in nearly regular six-sided tables, so

that it might be taken for cystine. If the fluid to be tested for uric acid contained a large quantity of metallic chlorides (for example serous exudations, &c.), the solution of uric acid ultimately obtained, contains, together with some other substances, much muriatic acid, and the residue of evaporation then sometimes becomes nearly black by the formation of humus-like matters. In this case the dry residue is again taken up in water, the colouring matter thrown down by acetate of lead, the filtrate freed from lead by sulphuretted hydrogen, and again evaporated. Sometimes the uric acid is mixed with that body resembling xanthine, to which the author has already repeatedly referred. This may be removed by washing with ammonia, but during this process some uric acid is also dissolved.—*Journ. für Prakt. Chemie*, lxxiii. p. 52.

Test for Cinchonine. By J. W. Bill.

In some investigations still in progress on some of the alkaloids, it became a matter of importance to discover a good test for cinchonine, delicate and characteristic, and distinguishing it especially from quinine.

We think we have found such a test, and as we believe it to be a reaction not before noticed, at least not applied to the above purpose, we will anticipate the results of the above-mentioned investigations, and give the test by itself.

When ferrocyanide of potassium is added to a salt of quinine in the cold, a yellowish white cloudy precipitate falls, provided the ferrocyanide be not added in excess; otherwise nothing characteristic results. This precipitate is soluble by heat, and readily so in solutions of ferrocyanide of potassium without any subsequent change occurring in the solution. If ferrocyanide of potassium be added to a soluble salt of cinchonine, whether added in excess or not, whether added to a strong or a weak solution, a yellow white curdy precipitate falls. If a very gentle heat be now applied, this precipitate dissolves, but as the liquid cools again, a crop of splendid yellow (gold-yellow) crystals falls so abundantly as sometimes to give a gelatinous appearance to the mass. These crystals are flat plates, cuneiform in shape, a pure lemon-yellow in colour, and superimposed one upon the other in the same way as are crystals of nitrate of urea. The crystals are best observed under a low magnifying power, fifty diameters, and will then be found such as we have described them. The *precipitate* is not soluble in excess of ferrocyanide of potassium, but like this the latter is decomposed by boiling with mineral acids. This test for cinchonine is a very delicate one, not less so than that by the biniodide of potassium, and is far more characteristic, since none of the alkaloids manifest the reaction except cinchonine. In practice it will be well, for obvious reasons, to use a slight excess of ferrocyanide of potassium, as little excess of acid as possible, and to heat the liquid *very* gently after the first precipitate has fallen.—Silliman's *American Journal for July* 1858.

Some New Facts with regard to Schweizer's Test.
By Professor SCHLOSSBERGER.

Schweizer's statements with regard to the solubility of woody fibre in ammoniacal solution of oxide of copper with the limitations and extensions of Cramer, have been almost entirely confirmed by the author. The new facts relate especially to the remarkable influence of many salts, and also of sugar and mucus upon the cellulose in solution or to be dissolved. These are followed by certain observations upon silk dissolved in CuO, NH^3, and upon the behaviour of some other organic matters to Schweizer's test.

1. The solvent or swelling action of CuO, NH^3 is greatly diminished or entirely removed by the presence of salts. The author was led to this discovery by the observation that a clear mixture of sulphate of copper and ammonia leaves cotton or Swedish paper quite uninjured even after standing for several days with frequent agitation. Cotton which had been soaked in a solution of $ClNa, NO^5 NH^4 O$, also resisted the well-prepared reagent so completely, as not even to swell up in it. From this is derived the prescription for the most advantageous mode of preparing the reagent:—Freshly precipitated and well washed CuO, HO is dissolved in concentrated ammonia; the greater the amount of CuO in it, the greater and more rapid is the solvent or swelling action. If a solution of $SO^3 CuO$ be added to a solution of cellulose in the reagent, the precipitate which is first formed is again dissolved, but another flocculent one is soon produced; this does not disappear again in an excess of ammonia or in acid,—it is cellulose.

2. The solution of cellulose, when perfectly clear, filterable, and presenting no solid constituents under the microscope, is immediately precipitated on the addition of concentrated solutions of alkaline salts. In this way a saturated solution of cellulose throws down a large quantity of a pale blue, flocculent-fibrous mass, which is amorphous under the microscope; this mass, when washed, is amorphous cellulose, insoluble in water and acids, and the supernatant fluid contains scarcely a trace of organic matter.

3. Honey, or a concentrated solution of gum-arabic or dextrine in water, precipitates the concentrated solution of cellulose just as completely and almost more rapidly. In this case also the precipitate is amorphous, which is a fresh proof that the cellulose was actually dissolved in the reagent, and not merely enormously swelled.

4. A considerable amount of Cu is essential to the efficacy of the reagent; the strongest aqueous ammonia has no action, and does not even cause swelling when it is too poor in Cu. On the other hand, a perfectly clear concentrated solution of cellulose in the reagent soon becomes turbid when greatly diluted with distilled water, and deposits pale flakes, which increase the longer it stands; this is the case even in well-stoppered bottles, and consequently when the evaporation of NH^3 is prevented.

5. The cellulose is evidently soluble as such in the reagent. If it be again separated therefrom by salt, sugar or acid, and washed,

it is insoluble in water, and does not even swell up in it (therefore it is not a kind of gum); it then gives no blue colour with iodine, but becomes beautifully blue with iodine and SO^3. The solution of cellulose when boiled, gives no precipitate of protoxide, but only gradually produces a pale blue turbidity; if potash be then added, and the boiling be continued, black CuO is at last produced. If the solution of cellulose be mixed with Barreswil's fluid, and boiled, no reduction of Cu^2O takes place even then. If the solution of cellulose precipitated by sugar, be boiled together with the precipitate, the blue colour is gradually lost entirely, the precipitate becomes yellow or colourless, appears coarsely fibrous, and has also lost all blue colour. It still gives the reaction of cellulose with iodine and SO^3.

6. A saturated solution of cellulose may be filtered through paper, although with great difficulty. The films which it furnishes by desiccation on glass, exhibit no structure under the microscope, and nothing like a cohesion similar to that of collodion. Nitrocellulose (gun-cotton) and dried collodion are insoluble in the reagent.

7. Chloroform or æther, agitated with the solution of cellulose, do not mix with it, and separate nothing from it. Alcohol, on the contrary, which mixes with the solution, throws down flakes, which do not again dissolve in water. Concentrated solution of urea does not precipitate the cellulose.

8. Potato-starch, which swells up extraordinarily even in the cold in CuO, NH^3, becomes again somewhat diminished in volume when washed with water. It is not dissolved even by heating with the reagent.

9. Inuline dissolves by degrees, without swelling, as has already been stated by Cramer. It was, however, very remarkable to observe that sometimes in the course of a few hours, but always in the course of a few days, a strong, blue, amorphous precipitate had separated again in the nearly clear blue solution; this was insoluble in water and NH^3, but soluble in tartaric acid and NO^5.

10. Chitine, far from dissolving in the reagent, does not swell in it even after standing for several weeks and being heated in it. Conchioline, byssus, the material of the air-bladders of *Velella* and the scales of ichthyosis remained equally unaltered. The cell membrane of the vesicles of yeast were also unattacked by the reagent. The cellulose in the mantle of the *Ascidia* also opposed an obstinate resistance to its action.

11. When silk was treated with CuO, NH^3 under the microscope, exactly the same swelling up, and analogous vermicular movements of the fibres were observed, as were formerly described with NiO, NH^3. The brown colour alone was wanting. The solution of silk in Schweizer's reagent is blue, in the author's brownish yellow. Salts, sugar, and gum either do not precipitate the cupreous solution of silk at all, or very imperfectly (this is a distinction from solution of cellulose); the solution of silk also exhibits a violet tint in the blue, which is entirely wanting with cellulose. Even acids usually precipitate the solution of silk (in CuO, NH^3) very imper-

fectly. If the solution be mixed with honey, and boiled, it acquires a yellow and afterwards a brownish-red colour, but only deposits scanty flakes.

Whether the NH^3 in Schweizer's and the author's reagents may be replaced by its organic homologues, still retaining the solvent power, remains to be decided by further experiments.—*Journal für Prakt. Chemie*, lxxiii. p. 371.

On the Solubility of Sulphate of Strontia in Nitric Acid, Muriatic Acid, and Acetic Acid. By R. Fresenius.

According to the author's previous experiments, 1 part of sulphate of strontia dissolves in 11,000 to 12,000 parts of water containing a little muriatic and sulphuric acid, that is, in a fluid such as is obtained when chloride of strontium is dissolved in water and the strontia is precipitated by an excess of sulphuric acid. Sulphate of strontia is, however, unequally soluble in fluids containing a somewhat larger amount of nitric acid, muriatic acid, and even acetic acid. This must be taken into consideration in analyses.

a. Pure freshly precipitated sulphate of strontia was digested in the cold for two days with dilute sulphuric acid of spec. grav. 4·8. 150 grms. of the filtrate left 0·3451 grm., so that 1 part dissolved in 435 parts. In a second experiment the proportion was 1 : 429. The average is

1 : 432.

b. Another portion of sulphate of strontia was digested in the cold for two days with dilute muriatic acid of spec. grav. 8·5. 100 grms. left 0·2115, and another 100 grms. 0·2104 grm. The average solubility of sulphate of strontia in muriatic acid of the above strength was therefore to be expressed by the proportion

1 : 474.

c. A third portion was digested in the cold for two days with pure dilute acetic acid containing 15·6 per cent. of hydrated acetic acid. 100 grms. of the filtrate left 0·0126 and 0·0129 grm. This gives the average,

1 : 7843.

Liebig's *Annalen*, May 1858, p. 220.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Process for Decolorizing the Fatty Oils. By C. Brunner.

As in all the fatty oils which he treated in the way described in the preceding article*, the author remarked, that after the evaporation of the æther, they were obtained of a much lighter colour than when first employed, in some cases even perfectly limpid, he endeavoured to discover a general process for bleaching the fatty oils in this way. This object was completely attained in many cases by proceeding as follows:—

* Chem. Gaz., p. 277.

The oil is made into an emulsion with water, to which the proper consistence is given by gum or starch-paste, and this emulsion is well worked up with thoroughly ignited charcoal, coarsely powdered and freed from fine dust by sifting. To 1 part of oil about 2 parts of charcoal powder are taken. The doughy mass is allowed to dry thoroughly at a temperature which should not exceed 212° F., and the oil is subsequently extracted with æther in the cold in a displacement apparatus. After this extract has deposited any charcoal-powder that may have passed through during the extraction, it is put into a retort, and the æther is distilled off in the water-bath. In this way olive-oil and walnut-oil are completely deprived of colour.

It might perhaps be supposed that the charcoal has a direct decolorizing action in this case upon the oil, just as in many cases it clears many aqueous fluids. This, however, is not the case. Oils left in contact with charcoal for weeks together did not undergo the least decolorization, even when they were dissolved in æther and digested with charcoal. The presence of the water contained in the emulsion appears first to give rise to the action. It is probable that by the preparation of the emulsion, the colouring matter, which does not belong to the oil itself, is taken up by the water and afterwards absorbed by the charcoal.

The action may be similar to that set up in the operation employed by painters to bleach oils, which consists in agitating the oil sufficiently with an equal volume of water, and exposing the mixture to the sun. The water, which soon separates again from the oil, appears turbid, and often mixed with slimy flakes. The operation is repeated for weeks, the water being frequently renewed, until it is no longer rendered turbid, and the oil appears limpid.

In the above process the essential part appears to be the complete desiccation of the charcoal mixed with the emulsion. If the oil be extracted with æther before this is the case, it is obtained again with its original colour.

Lastly, it is to be remarked that by this process the oils undergo a very remarkable thickening. Thus walnut-oil is obtained nearly of the consistence of butter.—*Bremer Mittheilungen*, Dec. 1857.

On the Fixation of Metallic Sulphurets in Cotton-printing. *By* Dr. H. Sacc.

The number of metallic colours employed in calico-printing is so small, that there is sufficient inducement to seek for new ones, as fashion daily requires patterns of more varied colours and more effect in the coloration.

Hydrated oxide of iron, manganese bistre, oxide of chrome, chromate of lead, ultramarine-blue and green, Schweinfurt-green, copper-iron green, and the sulphurets of arsenic and antimony are probably all the mineral dyes which are employed in calico-printing. Their use is, however, very limited, because some of them are difficult of fixation and others furnish unattractive tints; for this reason the reddish yellow, the sea-green from oxide of chrome, and the colours

fixed by white of egg are almost the only ones of the above-mentioned group which are still employed. From the circumstance that these colours are fixed with difficulty, the following experiments were made, with the view of fixing metallic colours upon calicoes by means of a current of steam.

Numerous attempts to fix solid, coloured metallic sulphurets of characteristic and fine tints upon the fibre proved failures; but satisfactory results were obtained by preparing the hyposulphites of those heavy metals whose sulphurets are not attacked by the weaker acids, such as cadmium, nickel, copper, lead, and mercury. Sulphuret of bismuth, protosulphuret and persulphuret of tin, and sulphuret of antimony were not adapted for this process, because the soluble salts of these metals are decomposed immediately when they are brought into contact with an alkaline hyposulphite, and thrown down in the form of perfectly insoluble sulphurets.

It is necessary that the metallic sulphuret should be formed upon the stuff itself, so that it must be employed in the form of a hyposulphite either in solution, or, at least, suspended; consequently, if the mixtures have been standing too long they become useless, because the metallic sulphuret is then already formed. After many trials the following proportions of the metallic salt and hyposulphite of soda proved to be the best.

It is to be noted preliminarily that the solution of gum contains 1 kilogrm. of gum in the litre of water, and the solution of hyposulphite of soda, 200 grms. of the solid salt in the litre.

Cadmium-yellow.—¼ litre of solution of gum is heated with 40 grms. of perchloride of cadmium, and ¼ litre of solution of hyposulphite of soda is added to the solution; the mixture is printed, steamed, and washed. It furnishes a very beautiful, solid, but unfortunately rather expensive yellow, which is but little changed even in the madder-bath.

Copper-green.—¼ litre of solution of gum is mixed with 25 grms. of sulphate of copper; the latter is dissolved by the aid of heat, and then ¼ litre of hyposulphite of soda is added. This green is very fine, and may be put into the madder-bath without undergoing any alteration; it is very uniform (when printed on a white ground it is better thickened with leicome than with gum), but it has the disadvantage, that when printed in warm weather it soon fades.

Nickel-gray.—¼ litre of solution of gum, 25 grms. of protochloride of nickel, and ¼ litre of hyposulphite of soda.

Lead-gray.—¼ litre of solution of gum, 25 grms. of nitrate or 50 grms. of acetate of lead, and ¼ litre of hyposulphite of soda. This gray may also be placed in the madder-bath without injury; the nickel-gray acquires a somewhat lilac colour by this treatment.

Mercury-gray.—¼ litre of solution of gum, 10 grms. of perchloride of mercury, and ¼ litre of hyposulphite of soda; or, to form chlorosulphuret of mercury, 50 grms. of perchloride of mercury instead of 10 grms.

These latter colours are very solid, but not easily prepared. The experiments will be further continued.—*Schweizer. Polytechn. Zeitschrift*, 1857, Bd. II. p. 175.

THE CHEMICAL GAZETTE.

No. CCCLXXXII.—September 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a new Acid obtained by the Oxidation of Malic Acid.

By M. DESSAIGNES.

UNDER the name of tartronic acid the author has described an acid obtained by the oxidation of tartaric acid in accordance with the following equation :—

$$C^8 H^{12} O^{12} = C^6 H^8 O^{10} + C^2 H^4 O^2.$$

Malic acid by a similar oxidation should furnish an acid $C^6 H^8 O^8$ in accordance with the equation

$$C^8 H^{12} O^{10} = C^6 H^8 O^8 + C^2 H^4 O^2.$$

This acid, identical or isomeric with Barral's nicotic acid, would be the member wanting in the oxalic series between oxalic and succinic acids; it would also present the same relations of composition with tartronic acid, as succinic acid with malic acid. This acid the author proposes to call *malonic acid*, until its identity with nicotic acid shall be proved.

It is produced by the oxidizing action of bichromate of potash upon free malic acid, but it is only a secondary product, and its amount is very small in proportion to that of the malic acid employed. A fragment of bichromate of potash is put into a rather weak solution of malic acid, and replaced when its action is exhausted; the heating of the mixture is prevented by placing the capsule containing it in cold water. The liquid evolves carbonic acid and an odour of formic acid, and becomes successively green, blue, and brown. The latter colour makes its appearance when the amount of bichromate added is about equal to that of the dry malic acid in the solution. Water is added, the fluid is moderately heated, and the whole of the oxide of chrome is precipitated by an excess of milk of lime. The green liquid separated from the precipitate by filtration and pressure, is precipitated by acetate of lead. The precipitate contains a considerable amount of chromate of lead, which is separated by nitric acid, which, when it is not added in excess, only dissolves the organic salt. This liquid is filtered, and three-fourths saturated with ammonia, when the lead-salt is repro-

duced in white flakes which contract considerably in the course of a few hours. This salt is washed and decomposed by sulphuretted hydrogen; the liquid, when filtered and concentrated by a gentle heat, furnishes crystalline laminæ floating on a greenish or bluish syrup which crystallizes with difficulty and confusedly. This syrup is malic acid retaining a little oxide of chrome; in the best conducted preparations it is at least equal in weight to the crystals. The latter are drained upon paper and purified by recrystallization.

Bimalate of lime is slowly oxidized by bichromate of potash, but in this reaction the formation of malonic acid was not observed. On the contrary, a large quantity of oxalate of lime was produced. Peroxide of lead also attacks free malic acid, but the new acid could not be found in the products of this reaction.

Malonic acid forms large rhombohedric crystals of a lamellar structure. It is very soluble in water and alcohol, and has a strongly acid taste. When heated to 212° F. it loses about ½ per cent. of interposed water and becomes opake; at 284° F. it fuses; at 302° F. it boils and evolves carbonic acid. It distils without residue; the condensed product is a mixture of acetic acid and unaltered malonic acid, which may easily be separated by a second distillation. The acetic acid was recognized by its physical properties and by the salt which it forms with oxide of lead. Its formation is explained by the following equation:—

$$C^6 H^8 O^8 = C^4 H^8 O^4 + C^2 O^4.$$

In the dry distillation of bimalonate of ammonia, acetate of ammonia was also produced, with carbonic acid and bicarbonate of ammonia.

When heated with concentrated sulphuric acid, the new acid is decomposed and becomes coloured. Its dilute solution forms a pulverulent precipitate with acetate of lead; with protonitrate of mercury a precipitate which becomes black when it is heated; and it reduces chloride of gold when boiled. Its concentrated solution does not precipitate acetate of potash; it precipitates the acetates of lime and baryta and nitrate of silver. The precipitates dissolve when water is added. The silver-salt does not become black when boiled. Neutral malonate of ammonia precipitates the salts of lime, baryta, silver, and mercury. It almost entirely decolorizes perchloride of iron, and does not prevent the precipitation of oxide of iron by ammonia added to the mixture of the two salts. The neutral salts of potash and ammonia are deliquescent, but they crystallize in dry air. The acid salts of the same bases crystallize readily in large, well-defined crystals. The neutral silver-salt forms a crystalline powder; the baryta-salt forms silky tufts, and the lime-salt small transparent needles.

Analysis gave—

	I.	II.	Calculated.
C	34·30	34·51	6 = 34·61
H	3·89	3·93	8 3·85
O	..	..	8 61·54

The silver-salt obtained from malonate of ammonia and nitrate of silver gave 67·65 and 67·97 per cent. of silver. The formula $C^6 H^4 Ag^2 O^8$ requires 67·92

The analogies of malonic acid with oxalic acid are evident, as the latter is decomposed into acetic and formic acids; the new acid produces carbonic and acetic acids; but towards succinic acid, which follows it in the series, it does not exhibit that gradation of chemical functions which indicates true homology.—*Comptes Rendus*, July 12, 1858, p. 76.

Note on Phthalamine, a New Alkali derived from Naphthaline.
By P. SCHUTZENBERGER *and* E. WILLM.

Béchamp has recently shown that naphthylamine might be obtained by the reduction of nitronaphthaline by means of protacetate of iron, or of a mixture of iron filings and acetic acid.

In studying some derivatives of the naphthylamine thus prepared, the authors obtained analytical results so little in accordance with theory, that they were led to believe that the product of this reaction was a mixture of naphthylamine and another base. On treating the crude product, after one distillation, with sulphuric acid, they separated two sulphates differing in their solubility in water, and both crystallizing in nacreous scales. The less soluble sulphate gave—

Water of crystallization	8·65
Carbon.....	62·3
Hydrogen	5·3
Sulphuric acid (SO^3).....	20·8

leading to the formula $C^{20} H^9 N (SO^3, HO) + 2Aq$, which is that of the sulphate of naphthylamine.

The more soluble sulphate gave—

Water of crystallization eliminable at 284° F. 8·06—8·15;

and the substance dried at this temperature furnished—

Carbon.....	48·19
Water	5·22

0·325 gr. of chloroplatinate of ammonia gave 0·162 of platinum, corresponding with 7·05 per cent. of nitrogen; and 100 parts gave 19·8 of sulphuric acid. These analyses lead to the formula

$C^{16} H^9 NO^4, SO^3, HO + 2Aq$ for the sulphate.

Theory,—

C	48·00
H.....	5·00
N.....	7·00
SO^3	20·00
HO	8·2

The base is precipitated in oleaginous drops rather more dense than water, when ammonia is added to the solution of the sulphate.

Its taste is that of naphthylamine; its salts do not redden so readily in the air. The authors propose to call it *phthalamine.*

The analyses were checked by those of the æthylic derivative obtained by heating a solution of phthalamine in iodide of æthyle to 212° F. In a few minutes the liquid forms a mass of foliated crystals of iodide of æthylophthalamine, which is easily purified by crystallization in water or alcohol. This salt becomes green in the air when in a moist state; it contains no water.

Its analysis gave—

	Found.	Calculated.
C	39·42	39·0
H	4·5	4·5
I	40·8	41·1

leading to the formula $C^{16} H^{8} (C^{4} H^{5}) NO^{4} I$.

The æthylated base when separated by ammonia is liquid and oleaginous, and boils at about 572° F. like phthalamine; it is alterable in the air, and has a burning taste.—*Comptes Rendus,* July 12, 1858, p. 82.

On a Colouring Matter extracted from Rhamnus frangula.

By T. L. Phipson.

After having extracted a colouring matter which I thought new, from the wood of the little baskets used for carrying Breton butter, I ascertained that these baskets were made of the twigs of *Rhamnus frangula,* and that M. Buchner of Munich had, in 1853, extracted from the root of this plant a yellow colouring matter which he called *rhamnoxanthine,* and which is identical with that I have extracted from the branches. My observations on the colouring principle confirm those of the chemist just named, at the same time completing them by new experiments which I have made upon rhamnoxanthine.

In the first place, I ascertained that this matter presents itself only in the layers of the liber and in the vessels of the medullary sheath of *Rhamnus frangula.* I have observed it also in *Rhamnus catharticus.* It exists in the state of solution in the plant. M. Buchner extracted it from the root by means of æther; it then contains a fat. In order to obtain it in a pure state, I immersed the branches in sulphuret of carbon, in which I allowed them to remain three or four days. The liquid, at the end of this time of a golden-yellow, was evaporated at ordinary temperatures, and the residue treated with cold alcohol, which dissolved the colouring matter, and left a peculiar brown fat. By evaporating the alcohol and dissolving the residue in æther, the colouring matter was obtained in the form of little shining crystals of a golden-yellow colour on the spontaneous evaporation of the æther.

Rhamnoxanthine is a ternary substance of the nature of resins or balsams. It is volatile (as was ascertained by M. Buchner), so that it may be obtained by carefully subliming the extract obtained from the branches by means of alcohol, æther, or bisulphide of carbon.

It is then converted into a white or yellowish vapour of an agreeable odour, which condenses like benzoic acid or alizarine. It is insoluble in water, most acids and salts; soluble in alkalies, æther, alcohol, and CS^2. Water precipitates it from the last three solutions.

Ammonia dissolves rhamnoxanthine, forming a magnificent red-purple solution; potash and soda behave pretty nearly in the same way; with the alkaline carbonates the colour is not so fine. The combinations of rhamnoxanthine with the alkalies are soluble in water, alcohol, and æther, but insoluble in CS^2. Acids destroy them, restoring the original yellow colour.

When concentrated sulphuric acid is poured upon rhamnoxanthine, this colouring principle changes immediately from its golden colour to a most beautiful emerald-green. This state lasts only an instant, and to preserve the new colour, the acid must be poured off directly. If the contact with the acid is prolonged, the beautiful green colour passes into purple, and it is finally dissolved in the acid with a red colour. By adding water to this solution, the original golden-yellow colour is restored. This green colour appears very stable, alkalies and dilute acids do not alter it; it differs essentially from chlorophyll, and may perhaps be the famous Chinese green (*vert de Chine*).

Under different deoxidizing influences rhamnoxanthine is transformed into a new brown colour. With oxides it forms lakes, the tints of which may be modified by a number of contrivances. Thus, by dissolving this principle in ammonia diluted with water, supersaturating with citric acid, and adding magnesia, I have obtained a very fine violet lake. With a combination of tin, I have obtained a kind of lake of a chocolate colour. With oxides in general, rhamnoxanthine may form lakes of red, brown, or yellow colour according to circumstances.

This colouring matter has much greater affinity for silk and wool than for cotton. By dyeing silk in a bath prepared with twigs of *Rhamnus frangula* and an aqueous solution of ammonia, subsequently acidified with citric acid, a fine golden-yellow tint is obtained. Wool is equally well dyed reddish-brown or yellow without the employment of mordants.—*Comptes Rendus*, July 26, 1858.

On Precipitated Oxide of Mercury.

By William Wallace, Ph.D., F.C.S., *Glasgow**.

Mercuric oxide, prepared by treating a solution of corrosive sublimate or mercuric nitrate with a caustic alkali, was formerly regarded as a hydrate, but Millon, Marchand, and Pelouze have declared it to be anhydrous. Schaffner† states, however, that the precipitated oxide contains 20 per cent. of water, and deduces from his analyses the formula HgO, 3HO.

Specimens of the oxide precipitated and dried at the temperature of the air, and at 212°, were carefully prepared. In no case did the precipitates lose more than about 1 per cent. on being heated to

* Communicated by the Author. † Ann. Ch. Pharm., li. 181.

incipient decomposition. The oxide appears to be decomposed with somewhat greater facility on the first application of a high temperature, than after having been strongly heated. This is probably owing to the conversion of the yellow oxide into the red by the action of heat.

Solubility in water.

1. Recently precipitated mercuric oxide was left in contact with water for several days, the mixture having been repeatedly stirred up. 200 cubic centims. of the fluid gave ·001 of oxide, or 1 part in 200,000 of water.

2. The oxide was boiled with water for some time, and the solution allowed to cool. 250 cubic centims. of the filtered liquid gave ·002 of oxide, or 1 part in 125,000 of water.

On some Platinum Bases. *By* C. GREVILLE WILLIAMS*.

In my paper "On the Volatile Bases produced by destructive distillation of Cinchonine†," I have alluded to a curious substance which made its appearance among the last crops of platinum-salts which had been subjected to fractional crystallization. It formed white needles which left metallic platinum on ignition. I concluded from some of its characters that it was a salt analogous to the bases of Reiset or Gros, but contaminated by an impurity. I have more than once endeavoured, without success, to reproduce this substance. My experiments have, however, led to the formation of two or three new bodies.

When dry chinoline is heated to ebullition with protochloride of platinum, combination ensues, a very pale yellow powder resulting. It is almost insoluble in water, but dissolves in a great excess of chinoline, and is re-precipitated by acids in an altered condition. To form the original substance, I cohobated chinoline in excess over protochloride of platinum for a considerable time. The undissolved portion was washed with æther to remove the excess of base, and dried at 100° C. The following result was obtained on a determination of the platinum:—

·2172 grm. of substance gave on ignition ·0816 platinum;

or, per cent.,

	Theory $C^{18}H^7N, PtCl$.
37·56	37·57.

From this it is evident that chinoline acts precisely like ammonia, producing a compound analogous to the green salt of Magnus, or the substance formed by Wurtz in acting with protochloride of platinum on methylamine. According to Gerhardt's views, the substance is the chloroplatinate of diplatosochinoline, and the formula being doubled, may be written $PtCl^3H, (C^{36}H^{13}Pt)N^2$; the

* Communicated by the Author.

† Trans. Royal Society of Edinburgh, vol. xxi. pt. 2. Chem. Gaz. 1853, p. 305.

portion between brackets being equivalent to two atoms of ammonia, in which one equivalent of hydrogen is replaced by platinum.

If the last-mentioned compound be dissolved with the aid of heat in a great excess of chinoline, and excess of hydrochloric acid be added to the filtered solution, a pale yellow precipitate is obtained; it is simply the original substance in combination with hydrochloric acid. The following is a determination of the platinum:—

·1084 grm. of substance gave ·0354 platinum;

or, per cent.,

	Theory ($C^{18}H^7N$, PtCl+HCl).
32·65	33·00

On boiling the above with chinoline, the hydrochloric acid is removed, and the original substance reproduced.

With the view of confirming the above results, I treated piperidine with protochloride of platinum and obtained a yellow powder. The reaction is very energetic, and much heat is evolved. The product dissolves in a very large quantity of boiling water, but on evaporation it separates in an altered condition. The original substance gave the annexed result on a platinum determination:—

·2012 grm. of substance gave on ignition ·0916 platinum;

or, per cent.,

	Theory $C^{10}H^{11}N$, PtCl.
45·53	45·10

From these experiments it appears that the compound ammonias, whether nitryles like chinoline, or imides like piperidine, behave towards protochloride of platinum precisely in the same manner as ammonia itself; the manner in which they unite not being influenced by the nature or number of the radicals contained in them.

On a Condition under which the Silicates of the Alkaline Earths are tolerably soluble. *By* P. Bolley.

That a precipitate is produced when lime-water or a dilute solution of a lime-salt is mixed with a solution of silicate of potash or soda, is an old and uncontradicted observation; and that this precipitate, as stated by Dalton, retains some alkali even after long washing, must be regarded as very probable from the analogy of other similar precipitations. According to Fuchs, when lime-water is treated with gelatinous silica, a body similar in composition to tabular-spar is thrown down. Silicate of lime is regarded as a difficultly soluble, or one might say insoluble body, as has been frequently remarked of late, especially in connexion with the "silicatization" of building stones and stereochromy, and the same is universally supposed to be the case with the compounds of magnesia, baryta and alumina with silicic acid. These few points include all the observations upon the phænomena which occur when the earthy salts come in contact with the alkaline silicates; at least I can nowhere find any mention of the following fact. If a solution of

soluble glass be added to lime-water or to a somewhat dilute solution of a lime-salt, a precipitate is produced, *which, however, disappears again entirely if the solution of soluble glass be added in excess.* The same thing occurs with salts of magnesia and baryta. This behaviour of the alkaline earths, leads almost necessarily to the assumption of the formation of soluble double salts, but the preparation of these in the solid state is met by difficulties at the very outset. I precipitated lime-water with a dilute solution of soluble glass, and added so much of the latter that only a part of the precipitate could be again dissolved. By long-continued shaking, leaving the precipitate to settle and pouring away the clear solution, no more alkali could occur in the latter than was absolutely necessary for the solution of the lime precipitate. The solution could not be evaporated by heat in order to obtain the compound in a solid state, because by this means, on the one hand, films were formed upon the surface, and on the other, after a certain degree of concentration had been attained, flakes were produced in its interior, indicating decomposition, but it had to be evaporated to dryness over sulphuric acid under the bell of the air-pump. The dried residue is amorphous, opaline, and tolerably transparent; it fuses into a permanently clear glass, and when reduced to a very fine powder, dissolves, although with difficulty, in muriatic acid. From a certain tenacity, which it does not lose without exposure to heat, it is difficult to reduce it to a fine powder. After calcination, its solubility in muriatic acid appears to be diminished. By long boiling with water the powder furnishes a little alkali to the latter; the alkaline reaction is very soon observable, but it was only after long boiling that I could detect lime and silicic acid in the fluid. This behaviour is probably to be explained by the portion of the alkali which is replaced by lime, and which remains mixed with the residue when evaporated under the air-pump, dissolving again when treated with water, whilst the double salt, when once separated in the solid state, is difficult of solution.

I have not yet succeeded (and this is intelligible under the last mentioned supposition) by the analysis of the solid residues obtained in the above way at different times, in arriving at a definite view of their composition.

One of these residues gave in two analyses:—

	I.	II.	Average.	Oxygen.
SiO^2	40·39	39·50	39·945	21·135
NaO	24·61	24·61 *	24·610	6·350
CaO	9·01	10·93	9·970	2·850
HO	25·99	24·96	24·975	

Another furnished:—

SiO^2	42·11	Oxygen	22·28
NaO	18·02	„	4·65
CaO	8·29	„	2·369
HO	31·58		

* Only determined in Analysis I.

The first of these precipitates was obtained with commercial soluble glass, the latter with a soda glass prepared in the laboratory in accordance with the directions of Fuchs.

In both cases the silica and lime were determined by decomposition with carbonate of soda, and the soda, in another portion, by hydrofluoric acid; decomposition by muriatic acid always left a silicic acid which contained some intermixed lime.

From these results no formula can be deduced at present; these double silicates are in the same position as the analogous ones (glasses) prepared in the dry way. There is no doubt that besides the circumstance already mentioned, the composition of the soluble glass, its dilution, and perhaps other conditions, also have an influence. I regard this side of the phænomena, however interesting it may be to discover new chemical compounds of accurately ascertained composition, as far less important than the observation that the silicates of the alkaline earths, which are so very widely diffused, may be easily brought to a soluble state.

With regard to the degree of solubility, I shall only say that the lime compound must be at least as soluble as sulphate of lime and lime itself, for the precipitation and re-solution of the precipitate is produced in solution of sulphate of lime and in lime-water by a few drops of concentrated solution of soluble glass, and a considerable quantity of water may be evaporated therefrom under the air-pump before any separation takes place. In a solution of chloride of calcium far richer in lime, the same thing takes place, so that not more than 100 parts of water are required for the solution of 1 part of silicate of lime in the presence of an alkaline silicate; and it would appear that the magnesia-salt is still more soluble.

In Bischoff's 'Textbook of Chemical and Physical Geology,' a work in which these conditions of solubility of mineral substances are referred to in great detail, we find it stated that 1 part of silicate of lime requires 5·383 to 19·395 parts of water, and 1 part of silicate of magnesia 32·376 to 90·600 parts of water for solution. In the discussion of the consequences which follow from the solubility of various mineral substances and their contact with water, the conditions of precipitability of the lime-salts by alkaline silicates, and the great tendency of silicic acid to combine with lime to form insoluble silicates, are emphatically mentioned.

If the power of interchange of a mineral substance and its part in the formation of the species of minerals and rocks be primarily dependent on its solubility in water, the observation here recorded cannot appear unimportant in a geological point of view, and perhaps the theory of the formation of the mineral skeleton of plants may also be thereby benefited.

When Liebig recommends the addition of lime-water to the water-glass prepared in the humid way from infusorial earth in order to purify it, it must not be forgotten that some of the lime is dissolved, but this is not injurious to the soluble glass in its applications.—Liebig's *Annalen*, May 1858, p. 223.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On two Ætherial Illuminating Materials, Pinoline and Oleone. *By* Dr. Hermann Vohl.

Pinoline.—The distillation of American resin, which is a mixture of the exuded resins of various species of *Pinus*, has been considerably extended of late, inasmuch as the products of distillation are employed in the preparation of the so-called patent grease for waggons and engines. The author has submitted a subsidiary product of this distillation, the so-called essence, to a minute investigation.

When the distilling vessel, which must be capable of holding about 1000 lbs., is charged with resin, the water existing in the resin, and with it a small quantity of a light essential oil, are expelled at the commencement of the distillation. The amount of the light oil, which is usually denominated "essence," averages 2 per cent. The water which accompanies the essence has a strong acid reaction, in consequence of its containing a considerable amount of acetic acid (many resins also furnish formic acid). The essence was usually rectified and sold as oil of turpentine. The high price of true oil of turpentine caused the purified essence, which was cheaper, to find a good market, and this would have been all very well, if this substance had been capable of the same applications as oil of turpentine. In general turpentine is employed in the preparation of varnish to dissolve the different resins, it also serves to thin oil colours, and cause them to dry rapidly. When oil of turpentine is exposed to the air, a portion of it will evaporate, whilst another portion will combine with the oxygen of the atmosphere, that is, become resinified, and consequently leave a varnish-like coat. Consequently when oil colours are diluted with oil of turpentine, no dullness or dryness of the colours will be produced thereby, unless the dilution has been carried too far.

If the behaviour of this essence be compared with that of oil of turpentine, the distinction is most striking. This essential oil is indeed subject to a resinification, but in a very small degree; consequently when this oil is employed as a substitute for oil of turpentine in diluting oil colours, less resin remains after desiccation, and the coating appears less shining and adhesive. This property of the essential oil of resin deprived it of its credit, and it became necessary to find another application for this subsidiary product, which is obtained in considerable quantities. From the author's investigation, the composition of the oil is nearly the same as that of oil of turpentine; and it was to be anticipated that, like the latter, it might be used for illuminating purposes. The "essence," which almost always has an acid reaction, was treated with solution of caustic alkali, and then blown off by steam.

The product thus obtained was limpid, and had an agreeab thyme-like odour, from which probably has originated the ide

entertained by the public that this oil is turpentine to which oil of thyme has been added in order to disguise the odour. The author called this oil *pinoline*, and under this name it was first brought into commerce as a fuel for lamps in 1856 by Brambach and Co., the possessors of a factory for the distillation of resin at Berge-Borbeck. It is burnt in lamps of peculiar construction, and gives a light similar to that of camphine. Pinoline, as already stated, is subject to resinization, by which it loses in value, inasmuch as the wick becomes impregnated with the resin formed, when the absorbing power is diminished and the lamp will smoke. These disadvantages render it necessary that the pinoline should be carefully protected from the atmosphere, and always sold freshly prepared. Its specific gravity is the same as that of camphine and oil of turpentine; it increases during resinification.

Oleone.—In large towns a considerable quantity of waste soap-water is always to be had, without taking into account the lyes obtained in the washing of wool, which are greatly impregnated with fat and oil. In towns where there is a manufacture of gas from resin, or where large establishments possess their own gas apparatus, the fat and oil of these waste fluids may always be made use of. But if a town be supplied with coal-gas, the employment of this waste fat for the production of gas is of no importance, and it is only used in the preparation of a very poor soap, which is by no means favourably distinguished by its unpleasant odour. In the year 1856, the author was commissioned to undertake an investigation of this fatty mass, and to find an advantageous use for it. He started from the point that it must be capable of conversion by dry distillation into an excellent ætherial illuminating material, and at the same time took into consideration the behaviour of the lime-salts of the organic acids under similar circumstances, when acetone-bodies of the respective acids are produced.

To obtain the fatty acids, the soapy fluids are mixed with a few hundredths of solution of chloride of calcium, by which all the fatty acids are separated in combination with lime in the form of a caseous precipitate (lime-soap). The precipitate is separated from the fluid by straining through a cloth, and freed from the greater part of the mechanically adherent water by a slight pressure. It is then mixed with 10 per cent. of unslaked, coarsely granular lime, and submitted to dry distillation, either in an iron retort or in a cast-iron pot with a flat cover. At the commencement of the distillation a quantity of aqueous vapours is produced, but these soon cease and give place to vapours with an empyreumatic odour. As soon as gases burning with a clear flame make their appearance, the true decomposition commences. By a good refrigeration the escape of the volatile oil is to be avoided.

When the gas burns only with a pale blue flame, and consists for the most part of carbonic oxide, the operation is completed; the receiver then contains an aqueous fluid upon which a considerable quantity of a butyraceous mass floats. This possesses a penetrating odour of burnt fat. After the water is removed from the olea-

ginous product, the latter is distilled in an iron or copper pot, by which one-third of a very volatile and permanently fluid oil is obtained; the second third is thickly fluid, and the last third solidifies in the cold. These three different products are treated in the way recommended by the author for photogene, with this difference, that instead of sulphuric acid of spec. grav. 1·834, acid of spec. grav. 1·704 is employed.

By distillation with steam a limpid, light oil of spec. grav. 0·800, possessing but little odour, is obtained; to this the author has given the name of *oleone*, with the view of indicating at once its origin, and the similarity of its composition to that of acetone. It is an excellent lamp fuel, and is not subject to become resinified. It may be burnt in the same lamps as photogene, camphine, and pinoline.

The second product, which is thickly fluid, is free from oxygen and not subject to oxidation in the air; it may be employed with advantage for greasing the fine parts of machinery, and may also be burnt. From the third product of the fractional distillation the author prepares a solid hydrocarbon resembling paraffine; it forms an excellent material for candles.—*Polyt. Journal*, cxlvii. p. 304.

Artificial Rose-water. By Professor WAGNER.

It is well known that the products of the spontaneous decomposition of salicylate of potash are distinguished by a peculiar rose-like odour. This salt is obtained by boiling oil of Winter-green (the essential oil of *Gaultheria procumbens*), which may now be obtained at a low price, with solution of potash. The mother-liquor poured away from the paste of crystals which is immediately formed, possesses a penetrating odour of roses, and when distilled with water, furnishes artificial rose-water.—Wagner's *Jahresber. über die Fortschritte der chemischen Technologie für* 1856, p. 260.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 17, 1858. (The Lord Wrottesley, President, in the Chair.)

"Researches on the Action of Ammonia on Glyoxal." By Dr. H. Debus.

If alcohol be slowly oxidized by nitric acid at ordinary temperatures, besides other substances, glyoxal, $C_2H_2O_2$, and glyoxylic acid, $C_2H_4O_4$*, are formed.

I have continued the investigation of these substances, and beg to lay before the Royal Society some of the more interesting results.

Glyoxal, of the consistency of ordinary syrup, is mixed with about three times its bulk of strong ammonia, and the mixture kept for twenty minutes at a temperature from 60° to 80° C. The liquid

* C=12, H=1, O=16.—Phil. Mag. Nov. 1856, and Jan. 1857.

now contains two organic bases—one in the shape of a crystalline precipitate, which I propose to call glycosine, and the other in solution, to which in this paper the name of glyoxaline will be applied. Besides these two substances, only a little formic acid and the excess of ammonia can be recognized in the liquid.

Glycosine=$C_6H_6N_4$. The crystals contained in the ammoniacal liquid are collected on a filter and washed with cold water. By dissolving them in diluted hydrochloric acid, treating with charcoal, and adding ammonia to the decolorized solution, the glycosine is obtained as a colourless, crystalline precipitate. The crystals are little prisms, tasteless, inodorous, and only soluble in a great quantity of boiling water. They become very electric when rubbed in a mortar. A little glycosine placed between two watch-glasses and heated on a sand-bath, sublimes without leaving a residue, and produces magnificent prismatic needles, sometimes half an inch in length. It forms salts with acids, which generally crystallize well. The chloride has a great tendency to form double salts with the chlorides of copper, mercury, and platinum.

Chloroplatinate, $C_6H_6N_4+2(H\,Cl\,Pt\,Cl_2)$, forms a fine yellow crystalline powder, soluble with difficulty in water. An excess of water seems to abstract bichloride of platinum and hydrochloric acid. Glycosine is formed from ammonia and glyoxal according to the equation—

$$\underbrace{3(C_2H_2O_2)}_{\text{Glyoxal.}}+4NH_3=\underbrace{C_6H_6N_4}_{\text{Glycosine.}}+\underbrace{6H_2O}_{\text{Water.}}$$

I showed on another occasion, that glyoxal has the properties of an aldehyde. Its behaviour towards ammonia confirms my former conclusions. The formation of amarine, from oil of bitter almonds, of acetonine from acetone and ammonia, takes place in a similar manner:—

$$3(C_7H_6O)+2NH_3=\underbrace{C_{21}H_{18}N_2}_{\text{Amarine.}}+3H_2O$$

$$3(C_3H_6O)+2NH_3=\underbrace{C_9H_{18}N_2}_{\text{Acetonine.}}+3H_2O$$

In all other known cases, when from an aldehyde or the chloride of an alcohol radical and ammonia, a basic substance is formed, one or two equivalents of ammonia participate in the reaction.

If ammonia and glyoxal decompose each other, four equivalents of the first transfer their nitrogen to one equivalent of the base produced. The direct derivation from ammonia of a base which contains four equivalents of nitrogen, seems to me to be very interesting.

The rational formula of glycosine is probably

$$N_4\left\{\begin{matrix}C_2H_2\\C_2H_2\\C_2H_2\end{matrix}\right.$$

C_2H_2 being equivalent to H_4.

It is worthy of notice, that in chemical decompositions very often three equivalents of an aldehyde unite and act like one molecule. I will only mention, as examples, mesitylene, acetonia, thialdine, hydrosalicylamide, and amarine.

Glyoxaline=$C_3H_4N_2$ is obtained as binoxalate from the mother-liquor of glycosine, if, after expelling the ammonia by gentle heating, an excess of oxalic acid is added. The binoxalate crystallizes very well and may be purified easily. The composition of it is expressed by the formula $C_3H_4N_2+C_2H_2O_4$. The base is obtained from this salt by treating it with carbonate of lime, and evaporating the filtrate from the oxalate of lime to the consistency of a strong syrup.

Glyoxaline crystallizes with difficulty in prismatic crystals, radiating from one centre. It is easily soluble in water, has a strong alkaline reaction, neutralizes acids perfectly, but does not appear to form a compound with carbonic acid. It melts easily, smells like fish, and evaporates at a higher temperature in dense white fumes. Chloride of copper forms a precipitate with glyoxaline, which is soluble in an excess of the base.

The chloroplatinate, $C_3H_4N_2+HCl\,PtCl_2$, crystallizes in large red prisms, and is easily soluble in hot water.

The formation of glyoxaline takes place according to the following equation:—

$$\underbrace{2(C_2H_2O_2)}_{\text{Glyoxal.}}+2NH_3=\underbrace{C_3H_4N_2}_{\text{Glyoxaline.}}+\underbrace{CH_2O_2}_{\text{Formic acid.}}+\underbrace{2H_2O}_{\text{Water.}}$$

Glyoxaline is homologous with sinnamine.

"On the Properties of Electro-deposited Antimony." By George Gore, Esq.

In this paper the following additional information is given respecting this singular substance.

The change observed in it is shown not to be an exercise of the force of cohesion, because the amount of heat evolved by the powdered metal is not sensibly different from that set free by the substance in its coherent massive state.

The thermic discharge is not limited to a particular temperature, but commences between 170° and 190° Fahr., and increases in rapidity to some point above 212° Fahr., when it becomes sudden.

The heat may be discharged either suddenly or gradually, according to the amount to be discharged in relation to the amount of cooling influences present.

The specific heat of the unchanged metal was found to be =0·06312; and of the same specimens, after being *gradually* discharged, the specific heat was not sensibly different. But the specific heat of the substance, after *sudden* discharge, was found to be=0·0543.

The total amount of heat evolved by the substance during its change was sufficient to raise the temperature of its own weight of ordinary antimony (sp. heat=0·0508) about 650° Fahr.

The evolution of vapour which generally occurs during the change

is a result of the molecular heat acting upon the terchloride of antimony contained in the substance. It occurs when a sufficient temperature is produced either by internal or external causes, and does not occur when the molecular discharge is gradual and the temperature is not sufficiently raised; in such cases the weight of the substance remains unaltered.

The substance, as usually produced from ordinary muriate of antimony, or from a mixture of that substance and tartar-emetic, contains small quantities of nearly all the ingredients and impurities of the depositing liquid.

The pure substance deposited upon sheets of platinum, in a solution of pure hydrochloric acid three-fourths saturated with pure oxide of antimony, with an anode of pure antimony, exhibited no material difference in properties from the less pure variety.

Two analyses of the pure unchanged substance gave the following per-centages:—

No. 1.		No. 2.	
Sb	93·36	Sb	93·51
$SbCl^3$ ...	5·98 } =6·44	$SbCl^3$ ...	6·03 } =6·24
HCl.....	0·46 }	HCl.....	0·21 }
	99·80		99·75

A trace of water contained in them was not estimated.

Solvents removed the chloride of antimony from the powdered substance much more readily *after* the thermic discharge than *before* it.

Differences of physical appearance were detected in the changed and unchanged substance in the state of powder under a microscope; the surfaces of the latter were *smooth* and brilliant, whilst those of the former were *granular* and less bright. No mechanical mixture could be detected in the changed powder.

From the various experiments detailed in the paper, it appears that the substance in question is a feeble chemical compound of antimony and acid hydrochlorate of terchloride of antimony, apparently in variable proportions, decomposable by heat, and that the change observed in it, in cases of *gradual* discharge, consists of a molecular alteration, attended by weakened chemical affinity, and by evolution of heat; but in cases of *sudden* discharge the evolved heat produces a partial chemical decomposition, which is of greater or less extent, according to the temperature acquired.

A portion of the powdered unchanged substance, digested sixty-three days with an aqueous solution of caustic potash, lost 2·95 per cent. in weight, but still retained about $\frac{3}{4}$ths of its heating power. A second portion, digested fifty-six days with strong hydrochloric acid, lost 6·66 per cent. and all its heating power.

Exposure to light did not destroy the heating power of the powdered substance.

By depositing the grey variety of antimony into mercury, a pasty compound of the two metals was formed. The amorphous variety did not combine with mercury under similar circumstances.

An acid solution of fluoride of antimony yielded by electro-deposition grey crystalline antimony not possessing the heating power.

"On the Action of Bile upon Fats; with Additional Observations on Excretine." By W. Marcet, M.D., F.R.S.

Having formerly observed and communicated to the Société de Biologie of Paris, that by heating a solution of neutral tribasic phosphate of soda ($2NaO . HO . PO_5$) mixed with animal fatty acids, an emulsion was obtained attended with the formation of a small quantity of soap, while no such action occurred if neutral fats were used instead of fatty acids, I was induced to inquire into the nature of the action of bile on neutral fats and fatty acids (sheep's bile being used), with the final object of throwing, if possible, some additional light on the digestion of fats. These investigations led to the following results:—

1. A mixture of bile and neutral fats (stearine, oleine and margarine), heated to a temperature above the fusing-point of the fat, undergoes no change, and no chemical action takes place.

2. A mixture of bile and fatty acids (stearic, oleic, and margaric acids), heated to a temperature above the fusing-point of the fatty acids, is transformed into a solution, a very few and minute globules only of fat remaining unacted upon from the presence of oleic acid. This solution becomes a perfect emulsion on cooling, and is attended with a chemical decomposition of the bile; and further, if the emulsion of bile and fatty acids be filtered when quite cold, and the residue on the filter thoroughly washed with distilled water, the filtrate and washings mixed together again possess the property of forming an emulsion with another quantity of fatty acids, being also at the same time partly decomposed, although in the previous operation the bile appeared to have exhausted its power on the fatty acids. The filtrate and washings from this second operation again act upon a fresh quantity of fatty acids, and so on; only in every subsequent operation the proportion of emulsion obtained appears to diminish, and the induced chemical decomposition to be lessened.

3. Pure oleic acid, when agitated with bile, cold or hot, produces no emulsion or chemical action whatever.

4. The stomach during digestion has the power of decomposing the fats contained in the food into fatty acids, fats acquiring thereby the property of being acted upon chemically by the bile, and of being transformed into an emulsion.

The chemical action, or saponification, induced by the fatty acids under the above circumstances, was proved by the mixture acquiring a strong acid reaction; and it was further observed that the acid filtrate from the cold emulsion was not precipitated by hydrochloric acid, showing apparently that fatty acids exert on bile a chemical decomposition at least as extensive as hydrochloric acid. With the view of determining precisely the amount of soap formed, a method of analysis was adopted calculated to indicate the proportion of fatty acid remaining unacted upon by the bile: the difference between the fatty acids used and the result of the above operation was equal to the weight of the fatty acids saponified. It was found, in three analyses, that the mixture of bile and fatty acids being exposed for three

hours (in Analysis II. for 3½ hours) to the heat of an open water-bath, contained an amount of soap in which the proportion of fatty acids was 30·21 per cent., 20·5 per cent., 11·5 per cent. of that employed in the analysis. The filtrate from the emulsion in analysis No. II., mixed with the solution obtained by washing the emulsion with distilled water, was treated for three hours on the water-bath with a fresh quantity of fatty acids, which operation yielded a proportion of fatty acid saponified equal to 12·7 per cent. of that used in the analysis. Finally, the filtrate and washings obtained in this last group were mixed with another quantity of fatty acids, and exposed for three hours to the heat of the water-bath, in which case the proportion of fatty acid saponified was equal to 3·8 per cent. of that used in the analysis. The various operations had been attended with the formation of an emulsion.

In order to be certain that, after exposing a mixture of bile and fatty acids to the heat of a water-bath for three hours, the chemical action thus induced was completely exhausted, two analyses were undertaken according to the process just mentioned, and with bile from the same gall-bladder; but in one operation the mixture was heated for three hours, and in the other for six hours: the proportion of fatty acid saponified was the same in both cases, showing that after three hours the bile had ceased to act on the fatty acids.

Having obtained the above results, an inquiry was next undertaken respecting the state of the fats of food in the stomach during digestion. For this purpose the contents of the stomach of several dogs, fed with cooked meat and neutral sheep's fat, were examined at different stages of digestion; the acids of the stomach soluble in water were removed by protracted washings with distilled water, and the residue being treated with alcohol and ether, yielded solutions found to contain fatty acids. In some cases the contents of the stomach were first treated with alcohol, and the fatty matters thus obtained subsequently washed with distilled water, and finally again dissolved in alcohol and ether. These analyses constantly yielded fatty acids, which, when heated with fresh sheep's bile, were found to dissolve and produce an emulsion.

In order to determine whether the cooking of the meat with which the dogs had been fed had transformed any of the neutral fats into fatty acids, a sample of roast meat was mixed and washed with distilled water until the washings had completely lost their acid reaction; the meat was then mixed with alcohol and allowed to stand for more than a week. After that time the fluid was found to be perfectly neutral, showing that no fatty acids had been formed.

From these researches it appears that the presence of bile in the intestines is closely connected with the digestion of fats.

The results of recent investigations on excretine show that this substance exists on an average in the proportion of 0·460 grm. for one evacuation when the excretine is impure, and of 0·184 grm. when it is pure. From the careful examination of the fæces of a child one year old, I have ascertained that they invariably contained

no excretine, but cholesterine; the proportion of the latter, purified by repeated crystallizations, being equal to 0·036 grm. in one evacuation, which number is, however, a very low estimate. Nothing in the food could account for this singular result. It is therefore most probable that excretine is only present in the evacuations of the full-grown or adult individual.

I have been most ably aided in these investigations by my assistant, Mr. Frederick Dupré, Ph.D.

"Contributions towards the History of the Diamides; Cyanate and Sulphocyanide of Phenyle." By A. W. Hofmann, Ph.D., F.R.S.

About ten years* ago, when engaged in the study of aniline, I discovered two beautiful crystalline compounds, carbanilide and sulphocarbanilide, which can be produced by a variety of processes. The former is best prepared by the action of phosgene-gas on aniline, while the latter is most readily and most abundantly procured by the action of bisulphide of carbon on aniline. The composition and the constitution of these bodies is indicated by the formulæ—

$$\text{Carbanilide} \ldots\ldots C_{26} H_{12} N_2 O_2 = \left.\begin{matrix}(C_2\ O_2)'' \\ (C_{12} H_5)_2 \\ H_2\end{matrix}\right\} N_2,$$

$$\text{Sulphocarbanilide} \ldots C_{26} H_{12} N_2 S_2 = \left.\begin{matrix}(C_2\ S_2)'' \\ (C_{12} H_5)_2 \\ H_2\end{matrix}\right\} N_2.$$

They may be viewed as derived from two molecules of ammonia (diammonia) in which two equivalents of hydrogen are replaced by two molecules of phenyle, and twoo ther equivalents by the biatomic molecules $C_2 O_2$ and $C_2 S_2$.

The two substances in question, as far as their formulæ are involved, obviously correspond to urea and sulphocyanide of ammonium:—

$$\text{Urea} \ldots\ldots\ldots\ldots\ldots\ldots C_2 H_4 N_2 O_2 = \left.\begin{matrix}(C_2 O_2)'' \\ H_2 \\ H_2\end{matrix}\right\} N_2,$$

$$\text{Sulphocyanide of ammonium} \ldots C_2 H_4 N_2 S_2 = \left.\begin{matrix}(C_2 S_2)'' \\ H_2 \\ H_2\end{matrix}\right\} N_2.$$

In their formation likewise a certain analogy with urea and sulphocyanide of ammonium may be recognized; for recent experiments have proved that urea is actually produced by the action of phosgene-gas on ammonia, while the formation of sulphocyanide of ammonium by means of ammonia and bisulphide of carbon is a long established fact. The analogy, however, seems to disappear altogether, if the chemical nature of the four bodies be compared, for while urea exhibits the deportment of a base, and the saline character of

* Journal of the Chemical Society, vol. ii. 36.

sulphocyanide of ammonium is so well defined, carbanilide and sulphocarbanilide are apparently perfectly indifferent substances.

Nevertheless, on considering the difference of the chemical properties of urea and sulphocyanide of ammonium, and on recollecting that the saline constitution of urea is much more hidden than that of sulphocyanide of ammonium, it appeared worth while to try whether the action of powerful agents would not reveal a similar, if I may use the term, saline construction in carbanilide and sulphocarbanilide. Experiment has realized this anticipation.

In the conception of the above view, I have endeavoured to split the two bodies in question according to the equations—

$$\underbrace{C_{26}H_{12}N_2O_2}_{\text{Carbanilide, Diphenyle-carbamide.}} = \underbrace{C_{12}H_7N}_{\text{Phenylamine.}} + \underbrace{C_{14}H_5NO_2}_{\text{Cyanate of phenyle.}},$$

and

$$\underbrace{C_{26}H_{12}N_2S_2}_{\text{Sulphocarbanilide, Diphenyle-sulphocarbamide.}} = \underbrace{C_{12}H_7N}_{\text{Phenylamine}} + \underbrace{C_{14}H_5NS_2}_{\text{Sulphocyanide of phenyle.}}$$

suggested by analogous changes of urea and sulphocyanide of ammonium:—

$$\underbrace{C_2H_4N_2O_2}_{\text{Urea.}} = H_3N + \underbrace{C_2HNO_2}_{\text{Cyanic acid.}},$$

$$\underbrace{C_2H_4N_2S_2}_{\text{Sulphocyanide of ammonium.}} = H_3N + \underbrace{C_2HNS_2}_{\text{Hydrosulphocyanic acid.}}$$

These reactions succeed without much difficulty. On submitting carbanilide and sulphocarbanilide to the action of agents capable of fixing aniline (anhydrous phosphoric acid, chloride of zinc, and even hydrochloric acid gas), the former yields *cyanate of phenyle*, a substance which I discovered many years ago among the products of decomposition of oxamelanile*, while the latter furnishes a remarkable body, *sulphocyanide of phenyle*, which had not been previously obtained.

The general features of cyanate of phenyle having been delineated in a former memoir, I have for the present been chiefly engaged with the examination of sulphocyanide of phenyle. This body, which is readily obtained in a state of absolute purity by rectification over anhydrous phosphoric acid, is a colourless transparent liquid of 1·135 density at 15°·5, and of a perfectly constant boiling-point at 222° C. under a pressure of $0^{m}\cdot762$. The odour is aromatic and pungent; it distantly resembles that of mustard; the body in question is in fact the mustard oil of the phenyle-series.

Mustard oil, sulphocyanide of allyle $C_8H_5NS_2 = C_6H_5, C_2NS_2$.
Sulphocyanide of phenyle ..... $C_{14}H_5NS_2 = C_{12}H_5, C_2NS_2$.

* Journal of the Chemical Society, vol. ii. 318.

Sulphocyanide of phenyle may be distilled with water, and even with hydrochloric acid, without undergoing any change. The alkalies, on the other hand, decompose it. Boiled with an alcoholic solution of potassa, it is first converted into sulphocarbanilide, and ultimately into carbanilide.

$$\underbrace{2C_{14}H_5NS}_{\text{Sulphocyanide of phenyle.}} + 4KO + 2HO = 2KS + K_2C_2O_6 + \underbrace{C_{26}H_{12}N_2S_2}_{\text{Sulphocarbanilide.}}$$

$$\underbrace{2C_{14}H_5NS_2}_{\text{Sulphocyanide of phenyle.}} + 6KO + 2HO = 4KS + K_2C_2O_6 + \underbrace{C_{26}H_{12}N_2O_2}_{\text{Carbanilide.}}$$

When gently warmed with phenylamine, sulphocyanide of phenyle is instantaneously converted into sulphocarbanilide,—

$$\underbrace{C_{14}H_5NS_2}_{\text{Sulphocyanide of phenyle.}} + \underbrace{C_{12}H_7N}_{\text{Phenylamine.}} = \underbrace{C_{26}H_{12}N_2S_2}_{\text{Sulphocarbanilide.}}$$

A similar reaction takes place with ammonia. An alcoholic solution of ammonia, when gently warmed with sulphocyanide of phenyle, readily solidifies into a crystalline compound, which may be obtained in beautiful needles by crystallization from boiling water.

The new body is formed according to the equation

$$\underbrace{C_{14}H_5NS_2}_{\text{Sulphocyanide of phenyle.}} + H_3N = \underbrace{C_{14}H_8N_2S_2}_{\text{Sulphophenylcarbamide.}}$$

This substance is the thiosinamine of the phenyle-series; like the latter, it possesses the characters of a weak base. I have not been able to obtain saline compounds with hydrochloric and sulphuric acids. It forms, however, compounds with nitrate of silver and bichloride of platinum. The latter has the usual composition, viz.—

$$C_{14}H_8N_2S_2, HCl, PtCl_2.$$

Boiled with nitrate of silver, the new compound loses its sulphur, which is replaced by oxygen, phenylcarbamide, $C_{14}H_8N_2O_2$, being produced, a substance which I described many years ago. Sulphocyanide of phenyle is acted upon by a great number of ammonias, with formation of bodies the composition of which is sufficiently pointed out by theory.

The mode of producing cyanate and sulphocyanide of phenyle, which I have described in the preceding paragraphs, deserves some notice, since the usual processes suggested by the experience in the methyle-, ethyle- and amyle-series, such as distillation of sulphophenylates with cyanates and sulphocyanides, have altogether failed in producing the desired result. The same reaction may be of course applied to tolylamine, cumylamine, naphthylamine, and all primary monamines.

THE CHEMICAL GAZETTE.

No. CCCLXXXIII.—October 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Transformation into Sugar of various immediate Principles contained in the Tissues of Invertebrate Animals. *By* M. BERTHELOT.

THE study of the immediate principles which fulfil the same physiological functions in different classes of animals, deserves to be especially pursued from the point of view of the comparison of the properties and composition of their principles with the office to which they are destined. Sometimes an immediate principle appears essential to the accomplishment of a determinate physiological function, and is endowed with the same fundamental properties in the whole series: the constituent principles of the nervous system are of this kind. Sometimes, on the contrary, the same function is executed by the aid of organs formed of totally distinct immediate principles; this is the character of the organic substances which in association with mineral salts constitute the skeleton of the various classes of animals.

The organic part of the skeleton of the Vertebrata is composed essentially of azotized matters insoluble in cold water, but soluble in alkalies, and very nearly approaching albumen and analogous bodies in their chemical characters. It is well known that gelatine is produced by the prolonged action of boiling water on these azotized matters.

The organic part of the skeleton of the Invertebrata is composed in great part of principles totally distinct from the gelatinous substances. The nature of these principles varies: sometimes they approximate to horny substances, sometimes they present a far stronger resistance to the action of reagents, and exhibit a remarkable analogy to the more essential immediate principles of vegetable tissues (Schmidt, Fremy, Schlossberger, &c.).

Such, for example, are chitine, one of the constituents of the skeleton of the Crustacea, the Arachnida, and Insects, and the prin-

cipal substance of the envelope of certain Tunicate mollusca. These two principles possess the following properties in common: they are insoluble in cold or boiling water, in alcohol, acetic acid, &c.; they are not attacked either by concentrated and boiling potash, or by dilute acids, and they do not present the characteristic reactions of the substances analogous to albumen. The principle of the Tunicata may be obtained free from nitrogen; in this state it has the same composition as cellulose, $C^{12} H^{10} O^{10}$, as proved by the experiments of M. Schmidt, confirmed by those of MM. Löwig, Kölliker, and Payen. Chitine, on the contrary, contains $\frac{1}{15}$th of its weight of nitrogen, which is not capable of being eliminated by reagents, according to the analyses of MM. Schmidt, Lehmann, and Schlossberger, and my own researches.

The foregoing characters are for the most part negative, and appear to apply, not to two veritable and definite immediate principles, but to two groups of principles, differing from each other in their very unequal resistance to the action of reagents. However this may be, we are led to connect these principles with those which constitute the tissues of vegetables. In fact, the principle of the Tunicata is isomeric with cellulose, and chitine presents in its properties and composition an evident analogy to these two substances.

Such approximations, however, founded upon the centesimal composition, do not establish any fundamental analogy between the chemical functions and reactions of the vegetable immediate principles and those of the constituent principles of the envelopes of the Invertebrata. More than this, experiments hitherto tried in this direction have remained fruitless. In order to demonstrate the existence of more real and complete bonds, I have endeavoured to make these latter principles undergo the most characteristic transformation of cellulose, the transformation in virtue of which this substance fixes the elements of water, and changes into fermentable sugar. I will describe *seriatim* the experiments I have made upon the principle of the Tunicata and upon chitine.

I am indebted to the kindness of M. Valenciennes for the envelopes of the Ascidia on which I operated (*Cynthia papillata*, Sav.). After having isolated them, boiled them for several hours in concentrated hydrochloric acid, then with a solution of potash of spec. grav. 1·282, I washed them with distilled water, dried, and submitted them to analysis. The numbers obtained agreed exactly with former analyses, and therefore with the composition of cellulose.

As the principle is totally different from vegetable cellulose in its physical and chemical properties, I think it necessary, to avoid confusion, to give it a distinct and unequivocal appellation; I propose the name *tunicine*.

Purified tunicine was submitted to a series of very diversified experiments to change it into sugar; but it opposed to the reagents a resistance far superior to that of the most coherent lignose. Thus it may be boiled for several weeks with dilute hydrochloric and sulphuric acids without sensibly altering. Fluoboric gas, which almost

instantaneously carbonizes all forms of cellulose, does not act in the cold upon dried tunicine. In short, the resistance of this substance to the action of reagents is so great, that in order to overcome it, it is requisite in almost all cases to employ agents which go too far, and are calculated not to produce sugar, but to destroy it, if already in existence.

However, I have succeeded in producing this transformation by the aid of a peculiar contrivance borrowed from industrial art, in which recourse is had to very powerful affinities acting only for a very short time. The dry tunicine is triturated with concentrated cold sulphuric acid; by degrees the substance becomes liquified without sensible coloration. The liquid is then transferred drop by drop into a hundred times its volume of boiling water, boiled for an hour, saturated with chalk, and the filtered liquid evaporated carefully, &c.; in this way is obtained a syrupy liquid, a mixture of sugar with an undetermined substance. This liquid energetically reduces tartrate of potash and copper, and is turned brown by boiling potash; diluted with water, and mixed with beer yeast, it ferments, producing pure carbonic acid and alcohol. These different characters establish the formation of a sugar analogous to glucose at the expense of the principle contained in the envelope of the Ascidia.

I have repeated the same experiment upon chitine. I operated on the chitine of the Spiny Lobster (*Palinurus vulgaris*) and that of cantharides. Whatever its derivation, and after the most careful purification, such as the employment of fusing potash, chitine retained 5 to 7 per cent. of nitrogen. This presence of nitrogen in chitine augments the interest of its conversion into sugar. In spite of the resistance of chitine to the action of reagents, a still greater resistance than that of tunicine, I have succeeded by the same process, in converting it into a sugar analogous to glucose, readily reducing tartrate of potash and copper, and fermenting with yeast to produce carbonic acid and alcohol.

These results establish a new and most intimate bond, founded upon a definite chemical transformation, between the immediate principle contained in the envelopes of the Invertebrata, and those which form the tissues of vegetables.—*Comptes Rendus*, August 2, 1858.

Investigation of Quinine. By P. Schutzenberger.

Sulphate of quinine, when boiled with a solution of nitrite of potash, gives rise to a rather brisk evolution of nitrogen. After the reaction, the liquid, on cooling and being treated with ammonia, furnished a white, granular, crystalline precipitate, which, when dissolved in alcohol and evaporated to dryness on the water-bath, left a transparent resinous residue. The contact of water rapidly changes this into small crystalline grains containing much water of crystallization. They fuse at 212° F. in their water, which they lose at 266° F., becoming changed into a colourless resinous mass, which remains solid at 284° F.

The analysis of the substance, dried at 302° F., gave—

C.....	70·32
H.....	7·4
N.....	6·36

leading to the formula

$$C^{40}H^{24}N^{2}O^{6} = \underbrace{C^{40}H^{24}N^{2}O^{4}}_{\text{Quinine.}} + 2O.$$

It is consequently oxyquinine.

The amount of platinum in the chloroplatinate is 25·90 per cent.; the formula $C^{40}H^{24}N^{2}O^{6}, 2(ClH, Cl^{2}Pt)$ requires 25·95 per cent.

This base therefore has the same capacity of saturation as quinine, which is also the case with other oxygenated alkaloids investigated by the author. It is but slightly soluble in water, soluble in alcohol and æther, and much less bitter than quinine. In its properties it approaches the stable hydrate of quinine described by the author in a previous memoir, except that it is crystallizable.

Igasurine ($C^{42}H^{20}N^{2}O^{8}+6Aq$), when treated with nitrous acid, also furnishes a product of oxidation, represented by the formula

$$C^{42}H^{30}N^{2}O^{18} = C^{42}H^{30}N^{2}O^{8} + 10O.$$

This base forms colourless needles, contains 8 equivs. of water of crystallization, and fuses in its water at 212° F.; it is coloured red by nitric acid.—*Comptes Rendus*, July 12, 1858, p. 81.

On the Amounts of Sulphuretted Hydrogen and Hydrocyanic Acid in Tobacco Smoke. *By* A. Vogel, Jun. *and* C. Reischauer.

If tobacco smoke be passed through an alcoholic solution of neutral or basic acetate of lead, the incurrent tube soon becomes blackened in a remarkable manner, whilst in the fluid itself a precipitate of carbonate of lead rendered brown by sulphuret of lead is deposited. To obtain the sulphuret of lead uncontaminated with carbonate of lead in the following quantitative investigations, the tobacco smoke was passed through an alcoholic solution of acetate of lead strongly acidified with acetic acid. The precipitate of sulphuret of lead was dried and weighed, after washing with alcohol.

1. Turkish tobacco, 3·4 grms. gave 7 milligrms. of sulphuret of lead.
2. „ „ 3·7 „ „ 7·5 „ „ „
3. German cigars, 3 „ „ 9 „ „ „

Hence the presence of sulphuretted hydrogen in tobacco smoke is unmistakeably proved. The presence of sulphuretted hydrogen in tobacco smoke may however be proved in a still more simple manner, by blowing the smoke through the cigar upon a piece of paper moistened with acetate of lead, when a brown colour is immediately produced on the spot touched by the smoke.

The well-known reaction of sulphuretted hydrogen upon nitroprusside of sodium is exhibited most characteristically when a few drops of a solution of that salt mixed with ammonia are put into a

test-tube and the tobacco smoke is introduced by a tube, which does not reach quite to the bottom of the test-tube. The walls of the glass moistened with the solution of nitroprusside of sodium, by shaking acquire a deep violet-red colour by the action of the sulphuretted hydrogen of the tobacco smoke. The above data show at the same time what influence the incineration of the parts of plants must have upon the accuracy of the determination of the sulphuric acid in the ashes.

In order to determine directly the loss of sulphuric acid in the ashes caused by the incineration, the amount of sulphuric acid in the tobacco ashes produced in experiment 1 was ascertained. From this it appeared that of 100 parts of sulphuric acid in the tobacco, 12·63 were evolved in the smoke in the form of sulphuretted hydrogen. This circumstance is consequently of importance in the determination of the sulphuric acid in incinerated parts of plants, and the more as a portion of the sulphuretted hydrogen also escapes observation in the upper part of the smoke of the burning tobacco.

After cyanogen compounds had been sought in vain, even in large quantities of the ashes of tobacco, the tobacco smoke itself was examined for cyanogen. The method of detecting hydrocyanic acid in the smoke is as follows:—Tobacco smoke is passed through a concentrated solution of caustic potash. The solution by this means acquires a slightly brownish colour, and when a turbidity is produced by dilution with water, it must be filtered. The solution is then mixed with protopersulphate of iron and heated. It is necessary to employ a spacious vessel for this purpose, as a strong evolution of carbonic acid takes place, especially at the boiling-point. The precipitate obtained is treated with an excess of chemically pure muriatic acid, when the precipitated oxide of iron is dissolved, leaving behind it prussian blue.

The separation of the prussian blue is facilitated by heating the solution; after filtration and complete washing with hot water, and afterwards with alcohol, it usually remains upon the filter of a dark blue colour. If, however, it be of a dingy green colour from the presence of empyreumatic constituents of the tobacco smoke, it must be freed from this impurity by agitation with æther and alcohol, when it always remains with its characteristic colour.

It is obtained most beautiful, when, after it has been washed as much as possible upon the filter, it is decomposed by solution of potash, and a protopersalt of iron is added to the solution filtered from the peroxide of iron, by which it is regenerated, freed from foreign intermixtures, after treatment with muriatic acid.

Two cigars, weighing together 10·6 grms., furnished 0·018 of prussian blue; and two cigars of another kind, weighing together 8·2 grms., gave 0·010 of prussian blue.

Amongst all the samples of tobacco investigated in the above manner by the authors, there was only one which gave an imponderable trace of prussian blue from 5 grms. This was a very old tobacco. All the rest distinctly showed the presence of prussian blue. The mode of smoking tobacco, whether in the form of a

cigar or in a pipe, in fact, the mode of combustion in general, appears to have an influence upon the formation of hydrocyanic acid in the smoke.—Dingler's *Polyt. Journal*, cxlviii. p. 231.

On Molybdenum. *By* H. Debray.

I. Under the name of *German molybdic acid*, we find in commerce a hydrated acid molybdate of soda which may readily serve for the preparation of molybdic acid and of the various compounds of molybdenum. Pure molybdic acid may be extracted from it by the following method:—

The acid molybdate of soda, mixed with its weight of powdered muriate of ammonia, is heated to redness in an earthen crucible. Chloride of sodium is produced, together with molybdic acid and metallic molybdenum. But these are not the only products of the reaction,—a considerable quantity of sulphuret of molybdenum is also formed, in consequence of the presence amongst the foreign salts of the German acid, of sulphate of soda. Sulphur having a special affinity for molybdenum, it is easy to understand that, under the influence of the ammoniacal salt, the sulphate and molybdate of soda may give origin to chloride of sodium and sulphuret of molybdenum. The final result of the operation is therefore a mixture of metal and insoluble oxide and sulphuret, which may be easily separated by means of water from the chloride of sodium formed, and from the soluble salts which contaminated the molybdate of soda employed. At first the water, which is strongly charged with salts, passes colourless. But when the quantity of dissolved matter diminishes, it acquires a bluish tint which announces the solution of a certain amount of oxide; the loss of metal thus caused is however too small to render it worth while to recover it from the washing-waters.

From their state of minute division the molybdenum, oxide, and sulphuret thus obtained burn with the greatest facility, even below a red heat. Their conversion into acid is therefore easy; the mixture is first roasted in a pot at a low temperature so as to lose no acid, which is volatile at a red heat; the product is then put into a platinum tray, which is heated to a good red heat in a slightly inclined earthen tube, of which the extremities are imperfectly stopped with two earthen plugs. Under the influence of the weak current of air which is set up in the tube, the molybdic acid is volatilized and deposited in the upper part of the tube in crystalline laminæ of great beauty, which may be compared in this respect to sublimed naphthaline.

To obtain a great quantity of acid very rapidly, the mixture may be acted upon by concentrated nitric acid. The action is very brisk at first, but in order to complete it, the acid must be heated to boiling for some time. This acid may also be pure, but the author has only employed it in the preparation of salts, and has always made use of the first method in order to procure absolutely pure acid.

II. Metallic molybdenum is obtained by reducing the acid by hydrogen at a low temperature at first, afterwards increased to a white heat in order to complete the operation. The metal thus obtained is in a state of very minute division; it presents no trace of fusion or even of agglomeration, as would be the case with platinum under the same circumstances. In this state it has been carefully studied by many chemists, especially by Bucholz and Berzelius.

This is not the case with the fused metal, which does not hitherto appear to have been obtained in sufficient purity. Bucholz, indeed, states that he has obtained molybdenum in rounded ingots of the weight of several grammes by heating bimolybdate of potash in a luted crucible in a good blast-furnace. The author believes that the metal obtained by Bucholz contained some foreign matter which increased its fusibility.

Thus, after vainly attempting to repeat the experiment of Bucholz, he tried to fuse the molybdenum reduced by hydrogen, in a charcoal crucible surrounded with lime, which was exposed to the temperature of a forge fed with charcoal. It will be remembered that H. Sainte-Claire Deville was able to fuse platinum and even quartz by means of this intense heat. The author, however, was unable either to fuse, or even to agglomerate the molybdenum by means of it. The metallic particles did not appear to have undergone the least approximation. Other experiments made with various fluxes did not succeed any better. The author then employed an apparatus in which charcoal crucibles, protected by a crucible of lime, might be heated by the oxyhydrogen blowpipe, and in which the temperature might be easily carried to the melting-point of rhodium. Under these circumstances, by employing various fixed fluxes, such as aluminate of lime, the fused metal was obtained, but not with certainty. The author found that at this temperature tungsten might be fused, although with more difficulty than molybdenum.

The metal obtained is not absolutely pure; analysis showed it to contain 4 to 5 per cent. of carbon, which must have increased its fusibility. But it is necessary to fuse it in charcoal crucibles, as they preserve it from the oxidizing action of the gaseous mixture with which it is surrounded, although unfortunately they convert it into cast metal. If the flame contained an excess of hydrogen, its temperature would be so much lowered that the fusion of the metal would become absolutely impossible.

The body obtained by the author is white, with a lustre approaching that of silver. It scratches glass and topaz with ease; the hardest steel has no action upon it; and it cannot be polished with powder of boron, but is slightly scratched by prolonged friction. Its density is 8·6, that is to say, the half of that of tungsten. Its chemical properties do not differ from those of the finely divided metal.

III. Of his investigation of the compounds of molybdenum, the author proposes to communicate the results shortly, but indicates a few in this note.

When gaseous muriatic acid is passed over molybdic acid gently heated (302°—392° F.), a white, crystalline compound, very volatile

and very soluble in water, is produced. Its composition is represented by the formula $MO^3\,HCl$, or $\left.\begin{matrix}MO^3\\Cl\end{matrix}\right\}HO$. Heat decomposes it into muriatic and molybdic acids, and it can only be volatilized in muriatic acid gas. If its solution be evaporated, amorphous molybdic acid alone is produced.

This tendency to combine with other acids is also shown towards phosphoric acid, which is capable of dissolving a very considerable quantity of non-volatilized molybdic acid. But the compound thus obtained does not furnish crystals; it merely becomes syrupous by evaporation. On saturating it with a solution of ammonia and cooling the liquid, fine crystals of a salt of the double acid are obtained; its composition appears to be very simple. The solution of this salt, treated with nitric acid, gives the yellow precipitate which originates, as has been shown by H. Rose, whenever phosphoric acid and a solution of molybdate of ammonia in nitric acid are brought in contact. This substance contains a certain quantity of ammonia, which may be removed by boiling in nitromuriatic acid. It then dissolves completely, and the liquid, when cooled, deposits magnificent yellow crystals of hydrated molybdic acid, MO^3, 2HO. These crystals are very soluble in water, so that they may be recrystallized, but the author found it impossible by this means to get rid of a small quantity of phosphoric acid (3 to 4 per cent.) which appears necessary for their formation.

On mixing, at a low temperature, concentrated solutions of hydrosulphate and molybdate of ammonia, there are produced in a few moments, needles of a fine golden-yellow colour, which appear to contain molybdic acid, hydrosulphuric acid, and ammonia. The author thinks that other acids may furnish analogous compounds.—*Comptes Rendus*, June 7, 1858, p. 1098.

On the Preparation of Laurostearine and Lauric Acid from the Oleum lauri unguinosum *of commerce.* *By* P. Bolley.

Marson directs the preparation of laurostearine from pounded laurel berries* by extraction with boiling alcohol, expression, filtration whilst hot, cooling, collecting the fat separated, dissolving it again, crystallizing it, &c. He says expressly that he did not succeed in preparing it in a pure state from the officinal oil of laurel berries. This is really difficult on account of the green colouring matter which accompanies the fat through all its solutions and depositions.

I succeeded in the following way in obtaining perfectly white laurostearine:—I exposed the green fat to the light of the sun in thin layers upon white porcelain plates covered with discs of glass, and observed in a few days that the green colour soon disappeared, and that brown solid fragments, which were nearly hard to the touch, were deposited in the clear fatty mass melted by the heat of the sun; from these the fat may easily be freed by filtration. By

* Liebig's Annalen, xli. p. 329.

dissolving the mass passing through the filter in alcohol, and setting it to crystallize, or precipitating it with water, the fat may be obtained perfectly white.—Liebig's *Annalen*, May 1858, p. 229.

Further Researches on Alcoholic Fermentation. *By* M. PASTEUR.

Contrary to the generally received opinion, I can affirm that not the smallest quantity of lactic acid is formed in the alcoholic fermentation; and whenever this acid is met with in such case, it is the result of two simultaneous and very distinct fermentations. Alcoholic fermentation is accompanied by lactic acid only in rare and exceptional circumstances, and when peculiar conditions, producible at will, have given origin to that ferment which I have made known under the name of *lactic yeast.*

This new yeast being formed of globules much smaller than those of the yeast of beer, it is easily ascertainable by the aid of the microscope if a mixture of the two yeasts exists, and by this we may even foretell the presence or absence of lactic acid.

A question naturally presents itself: it has been known from the time of Lavoisier, that in the alcoholic fermentation the liquid always acquires an acid reaction. If lactic acid is only formed exceptionally by the means I have just indicated, what is the cause of the constant acidity of the liquid? Repeated experiments enable me to assert that the acidity of the liquid in alcoholic fermentation is owing solely to succinic acid. The presence of this acid is not accidental, but constant; and if we neglect the volatile acids which are formed in what may be termed infinitely small quantities, we may say that succinic acid is the sole normal acid of the alcoholic fermentation. In whatever conditions I have operated hitherto, I have found succinic acid and glycerine as constant as carbonic acid and alcohol in relation to their existence as products of alcoholic fermentation.

Every one will understand the consequences contingent on these results. But in the discussion of them no one should be more reserved than myself.—*Comptes Rendus*, August 2, 1858.

On a Fat containing Phosphorus, in Peas. *By* Dr. W. KNOP.

In an investigation of the garden pea (seeds of the previous year or of former years, perfectly capable of germination), the author found 2·51 and 2·61 per cent. of a brown oil, exhibiting a golden-yellow colour in thin layers. After the saponification of about 0·8 grm. of this oil with potash, the soap was burnt with the addition of a great quantity of carbonate of soda and a little nitrate of potash in a silver crucible; it furnished a fused mass which contained phosphoric acid. This is dissolved in acetic acid, mixed with muriate of ammonia, supersaturated with acetic acid, and freed from traces of chloride of silver by filtration, when acetate of uranium at a boiling heat precipitates a ponderable quantity of phosphate of uranium and ammonia. The oil cannot be freed from its phosphorus by boiling

with water; the phosphoric acid consequently is not merely intermixed. Water takes up no trace of it; if it be subsequently saturated with chloride of sodium, the oil separates again completely from the water, and contains phosphorus after as well as before this treatment with water. We are therefore justified in regarding this oil as containing phosphorus, just as much as the fat of the same kind occurring in the brain and in the yolk of eggs. The analysis of the oil will be published hereafter; it gave 3·0 to 3·5 per cent. of phosphoric acid by the above treatment.—*Chemisches Central-Blatt*, June 30, 1858, p. 479.

ANALYTICAL CHEMISTRY.

On a new Mode of determining Copper. By F. Pisani.

When iodide of potassium is added to the solution of a salt of copper, a brownish-yellow precipitate is formed, which under the influence of a reducing body, such as sulphurous acid, becomes converted into protiodide, Cu^2I, presenting the aspect of a white powder insoluble in water. It is under this latter form that I determine the copper. The following are the details of the analysis:—

To the solution of copper, previously freed from all the metals whose iodides are insoluble, I add sulphurous acid, then, after having applied a gentle heat, iodide of potassium until the supernatant fluid has lost the colour due to the presence of copper and the formation of a precipitate ceases. The protiodide of copper being very dense settles readily, especially when heated, like chloride of silver. In this precipitation the sulphurous acid must always be in slight excess, to avoid the formation of the brown compound. After having heated the liquid nearly to boiling, it is filtered on a counterpoised filter. The precipitate is washed with hot water, and dried, and with the filter put into a stove heated to 230° or 248° F., after which the protiodide of copper is weighed; from its weight the quantity of metal is calculated.

During the filtration the filtered liquid must be set aside as long as it passes clear; for when the precipitate is washed, as it has the property of climbing up the filter, especially when it has not been well collected by ebullition, the liquid sometimes passes a little turbid, which renders it necessary to filter it again. Otherwise the filtration and washing are effected very rapidly.

When the solution of copper is made by nitric acid (as in the case of alloys and minerals), the employment of an excess of this acid must be avoided, for it would oxidize the sulphurous acid, and thus compel much of it to be added. In this case the excess of nitric acid may be neutralized by potash; then if the latter reagent has been employed in excess, it may be slightly acidified again with dilute sulphuric acid. The precipitation of copper by iodide of potassium is nearly complete, for I have ascertained that

there never remains more than 1 or 2 thousandths in the filtered liquids.

Analysis of Brass.—By this method of determining copper, when zinc is present at the same time, the separation of these two metals is perfectly effected, and there is no fear that zinc will remain with the copper, as is usually the case in other processes. After the determination of the zinc, it is well to ascertain that no copper remains with it, by treating the oxide of zinc with muriatic acid, and afterwards with ammonia. In case an appreciable quantity should remain, the filtered ammoniacal liquid is acidified by muriatic acid, and a little sulphuretted hydrogen is added to it. The sulphuret of copper, after being washed, is calcined and weighed. The oxide of copper thus obtained furnishes the quantity to be added to that already found. But in most cases this last operation may be dispensed with.

Separation of Copper and Cadmium.—The separation of copper and cadmium is also complete, and this method may be added to those already known for recognizing this metal in the presence of copper, or to separate it from the latter. For this purpose it is sufficient to precipitate the copper, as above described; then, after filtration, the cadmium is separated by sulphuretted hydrogen.—*Comptes Rendus*, August 16, 1858, p. 294.

Note on the Detection of Iodine by Starch.
By O. Henry *and* E. Humbert.

Chlorine which is employed to set free the iodine and render it capable of giving a blue colour with starch, has some advantages over the other oxidizing bodies which have been made use of for the same purpose, as by converting them into sulphates, it more readily destroys the sulphurets and sulphites, the presence of which might prevent the liberation of the iodine, and the production of a blue colour in the liquid. But an excess of it, which is difficult to avoid, even by operating with a very dilute solution of chlorine, often also has the effect of causing the disappearance of the coloration produced by the first addition of the reagent, in consequence of the conversion of the iodine into iodic acid or chloride of iodine. The action of a deoxidizing agent, such as sulphurous acid, for example, may again set free the iodine and render the liquid blue; but an excess of this reagent has also the effect of causing the disappearance of the coloration. This new obstacle may be avoided, and the blue tint which has disappeared may be reproduced permanently, by effecting the deoxidation by the agency of nascent hydrogen. If a few drops of sulphuric acid and a small fragment of zinc be added to the liquid treated with an excess of chlorine, and of which the transitory blue colour may have passed unperceived, the tint is seen to return, at the end of fifteen or twenty minutes, to a blue tint, which remains exactly the same, even after the lapse of forty-eight hours, notwithstanding the great excess of hydrogen evolved.

The iodide of cyanogen of which we have indicated the utility for extracting and converting into a volatile and perfectly recognizable compound the iodine contained in the residues in which it is sought for, does not require the employment of the solution of chlorine, and produces the blue tint in starch-water directly, by the simple addition of sulphuric acid and zinc.—*Comptes Rendus*, August 16, 1858, p. 298.

Ammoniacal Solution of Protoxide of Nickel, a Means of distinguishing Silk and Cotton. By Professor SCHLOSSBERGER.

The violet-blue solution of freshly precipitated hydrate of protoxide of nickel exerts an extremely remarkable action upon silk. If silk threads be brought in contact with a drop of this solution under the microscope, peculiar vermicular movements are observed in it, and at the same time they swell up considerably and acquire a yellow colour. Soon afterwards the outlines become pale, in part (with raw silk) accompanied by considerable inflations or ruptures of the external envelopes of the fibres, and finally complete solution takes place. If silk be thoroughly kneaded up in a test-glass by means of a glass rod with the blue solution of nickel, it soon becomes of a brownish-yellow colour, resembling that of hydrated oxide of iron; it then becomes slippery and gelatinous, and at last furnishes a brownish-yellow solution.

If the silk fibres be washed with water in the first stage of their alteration by the author's new reagent, all further action ceases; in later stages of change, they are also fixed by washing. The same thing is effected by a drop of weak acid, by the addition of which the fibre also loses somewhat in volume, and becomes colourless.

Solutions of alkaline salts do not precipitate the solution of silk, nor do solutions of sugar and gum. It is remarkable that a solution of $Cl\,NH^4$ restores the original violet-blue colour to the brownish yellow solution of silk in $NiO\,NH^3$, without separating anything. The solution of silk and nickel is abundantly precipitated by acids, and this precipitate (in colourless flakes of the aspect of hydrate of alumina) is permanent, when the acids are not too strong. The fluid exhibits a greenish colour.

Cellulose (cotton) is not at all altered, even by immersion for several days in the solution of $NiO\,NH^3$; after lying in it for three days, the fibres of cotton still presented their original form under the microscope, and there was no trace either of swelling or coloration. Potato-starch also did not swell up in it; inuline was gradually dissolved.

No analogous action has yet been produced upon silk by means of solutions of CoO, ZnO, and Al^2O^3 in NH^3. In the coloration, swelling, and solution of silk by NiO, it is essentially a matter of indifference whether the silk employed be raw silk, or silk deprived of its dressing by boiling.—*Journal für Praktische Chemie*, lxxiii. p. 369.

Note on the Use of the Molybdate of Ammonia Test for Phosphoric Acid. *By* J. W. Bill.

We observed on one occasion that on conducting the process for the detection of phosphoric acid in a liquid we were nearly sure contained it, that we obtained a green, a splendid chrome-green, instead of the characteristic yellow precipitate. This was observed in the laboratory of Mr. Henry Wurtz, who examined the liquid and corroborated an examination we had made proving that a soluble iodide was present as well as phosphoric acid. For a while we were puzzled to account for this phænomenon, but it appears to us that it may be explained thus.

The free nitric acid liberated some iodine, and this reduced the molybdate to the state of the molybdo-molybdate, $Mb^2 O^5$, and this in solution is a cobalt-blue. This blue liquid, on being mixed with the yellow precipitate, gave the green colour observed. Iodide of potassium and nitric acid when added to the yellow precipitate decompose it, forming the same green coloured liquid. If this is sealed up in a glass tube, in about three weeks large crystals of iodine will be found lining the sides of the tube, the liquid will have become brown-red in colour, and a gas will have been eliminated sufficient sometimes to have burst the tube. The reaction may be expressed in a formula thus: the yellow precipitate, the nitric acid and the iodide of potassium will give $2[NH^4 O, MbO^3] + 2[NO^5] + KI + PO^5 = Mb^2 O^5$ (molybdate of molybdenum) + $2(NH^4 O NO^5) + KO\,PO^5 + I$. — Silliman's *American Journal for July* 1858.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 17, 1858. (The Lord Wrottesley, President, in the Chair.)

"Action of Bibromide of Ethylene upon Aniline." By A. W. Hofmann, Ph.D., F.R.S.

While engaged in some experiments on the action of bibromid of ethylene on ammonia, a short account of which I have latel communicated to the Royal Society*, I induced Mr. Henry Bassett then working in my laboratory, to study the deportment of the same bromide with aniline, a characteristic representative of the class of primary monamines. In the following pages I propose to submit to the Society Mr. Bassett's observations, together with the results of a series of experiments which I carried out myself after Mr. Bassett by circumstances had been prevented from a further continuation of the inquiry.

A mixture of 1 volume of the bibromide of ethylene and 2 volumes of aniline, when exposed to the temperature of boiling water for an hour or two, solidifies into a crystalline mass of more or less solidity.

* Proceedings of the Royal Society, vol. ix. page 150.

This mass is chiefly hydrobromate of aniline; it contains, however, in addition, three new organic bases, partly free, partly in the form of hydrobromates. These substances are formed in very different quantities,—a beautiful crystalline body, difficultly soluble in alcohol, being invariably the chief product of the reaction, while the two other bases, the one solid but extremely soluble in alcohol, the other likewise solid but quite insoluble in this liquid, are found to be present in much smaller proportions.

The preparation, in a state of purity, of the principal product of the reaction presents no difficulty. The solid mass obtained by digesting bibromide of ethylene and aniline in the stated proportions is mixed with water, and submitted to distillation, when any bibromide left unchanged, together with some unaltered aniline, passes over. The residuary liquid is then mixed with a strong solution of potassa, which separates all the bases existing as hydrobromates in the form of a semi-solid resin. This is washed with water and then again submitted to distillation with water, when, together with more or less water, an additional quantity of aniline distils. The residuary mass, when treated with boiling (methylated) spirit, leaves the insoluble base as a white, flour-like powder, while the other two bases dissolve. On cooling, the solution deposits a beautiful crystallization of white needles, while the more soluble base remains dissolved in the spirit. The crystals are rather difficultly soluble in alcohol; two or three crystallizations from this solvent render them absolutely pure.

Thus obtained, the new base, for which, in accordance with the results of analysis, I propose the name *ethylene-phenylamine*, is a snow-white, inodorous and tasteless crystalline compound, of nacreous lustre, insoluble in water, soluble in boiling, less so in cold alcohol, soluble in ether. The solutions are without action on vegetable colours. The substance dissolves readily in hydrochloric, sulphuric and nitric acids, especially on gently heating the liquids, which on cooling deposit well crystallized saline compounds. The hydrochlorate yields yellow precipitates with bichloride of platinum and terchloride of gold. When exposed to the action of heat, ethylene-phenylamine fuses at 148° C.; at a temperature approaching 300° it begins to boil and to distil, the larger portion undergoing decomposition. Among the products of decomposition which are not yet sufficiently examined, considerable quantities of aniline make their appearance. The results obtained in the analysis of ethylene-phenylamine lead to the formula

$$C_{16} H_9 N$$

as the simplest molecular expression for this compound.

This formula is confirmed by the analysis of the hydrochlorate and of the platinum-salt, the preparation of which, on account of their instability, requires some management.

These salts contain respectively

Hydrochlorate.....$C_{16} H_9 N$, HCl.
Platinum-salt .....$C_{16} H_9 N$, HCl, $PtCl_2$.

The reaction which gives rise to ethylene-phenylamine is expressed by the following equation:—

$$\underbrace{2C_{12}H_7N}_{\text{Phenylamine.}} + \underbrace{C_4H_4Br_2}_{\substack{\text{Bibromide}\\\text{of ethylene.}}} = \underbrace{C_{12}H_7N, HBr}_{\substack{\text{Hydrobromate}\\\text{of phenylamine.}}} + \underbrace{C_{16}H_9N, HBr}_{\substack{\text{Hydrobromate of}\\\text{ethylene-phenylamine.}}}.$$

What is the constitution of this new base? This question could not be answered without further experiments, on account of the twofold nature of bibromide of ethylene. In many cases this remarkable compound exhibits the character of the hydrobromic ether of a biacid ethylene-alcohol, of $(C_4H_4)''Br_2$, whilst in the majority of reactions it splits into hydrobromic acid and the bromide C_4H_3Br, which might be considered as the hydrobromic ether of a monacid alcohol, $C_4H_4O_2$, homologous to allylic alcohol. It remained therefore uncertain whether the new basic compound retained the original molecule $(C_4H_4)''$ replacing 2 equivs. of hydrogen, or the modified molecule C_4H_3 replacing 1 equiv. of hydrogen. In other words, it had to be established by further experiments, whether the base was

$$\left.\begin{matrix}(C_4H_4)''\\C_{12}H_5\end{matrix}\right\} N = C_{16}H_9N, \text{ or}$$

$$\left.\begin{matrix}C_4H_3\\C_{12}H_5\\H\end{matrix}\right\} N = C_{16}H_9N.$$

The deportment of the substance with iodide of methyle and ethyle, which immediately will be mentioned somewhat more in detail, has decided in favour of the former view, and in accordance with it the name of the substance has been selected.

It deserves to be noticed, that there are already two other bases known which have exactly the same composition, the one obtained by M. Natanson in the reaction of bichloride of ethylene upon aniline, and described by him as *acetylaniline*, the other discovered by M. Dusart among the derivatives of nitronaphtaline and designated as phtalidine. It is only necessary superficially to glance at the description of these bodies in order to see that they are essentially different from ethylene-phenylamine. The constitution of acetylaniline and phtalidine has not been experimentally fixed. It is probable that Natanson's base contains the molecule C_4H_3 formerly called acetyle, but for which the more appropriate term vinyle has lately been proposed, while phtalidine probably derives from the hydrocarbon styrole or an isomeric body, so that the difference in the constitution of the three bodies would be expressed in the following formulæ:—

Phtalidine Styrylamine (?)	$\left.\begin{matrix}C_{16}H_7\\H\\H\end{matrix}\right\}$	N.
Acetylaniline Vinyl-phenylamine	$\left.\begin{matrix}C_4H_3\\C_{12}H_5\\H\end{matrix}\right\}$	N.
Ethylene-phenyl-amine	$\left.\begin{matrix}(C_4H_4)''\\C_{12}H_5\end{matrix}\right\}$	N.

I have already mentioned that the degree of substitution of ethylene-phenylamine was fixed by the deportment of this base with iodide of methyle and ethyle, bibromide of ethylene exerting no longer any influence upon it, even by protracted contact, at temperatures varying from 100° to 150° C.

A mixture of ethylene-phenylamine and iodide of methyle, on the other hand, when exposed for some hours to the temperature of boiling water, solidifies to a resinous mass, floating, together with a portion of unchanged base, in the excess of the iodide. Distillation with water separates the excess of iodide of methyle; and washing with cold water until the filtrate is no longer precipitated by an alkali removes any hydriodate of ethylene-phenylamine formed during the distillation. Lastly, by repeated crystallization of the resinous residue from boiling water, to which a small quantity of spirit may be added in the later stages (separation from ethylene-phenylamine), a perfectly crystalline, slightly yellowish iodine-compound is obtained, which may be dried without decomposition at 100°.

On analysis, this iodine-compound was found to have the remarkable composition

$$C_{34}H_{21}N_2I = \left.\begin{matrix} C_{16}H_9N \\ C_{16}H_9N \end{matrix}\right\} C_2H_3I.$$

Treated with oxide of silver, the solution of the iodide yields a powerfully alkaline liquid, possessing all the characters of the class of bodies of which hydrated oxide of tetrethylammonium is the type. On adding hydrochloric acid and bichloride of platinum, this liquid furnishes a pale yellow amorphous platinum-salt containing

$$C_{34}H_{21}N_2Cl, PtCl_2 = \left.\begin{matrix} C_{16}H_9N \\ C_{16}H_9N \end{matrix}\right\} C_2H_3Cl, PtCl_2.$$

A repetition of this experiment in the ethyle-series has given perfectly similar results. On account of the less powerful action of iodide of ethyle, the reaction requires longer digestion. The iodide formed is less soluble in boiling water than the corresponding methyle-compound, and therefore more difficult to separate from any ethylene-phenylamine which may have remained unchanged. When pure, the new iodide is a yellowish white substance crystallizing in needles. It fuses in the water-bath without decomposition to a yellow oil, which solidifies on cooling into a brittle crystalline mass.

On analysis, numbers were obtained corroborating in every respect the results furnished by the methyle-series. The iodide contains

$$C_{36}H_{23}N_2I = \left.\begin{matrix} C_{16}H_9N \\ C_{16}H_9N \end{matrix}\right\} C_4H_5I.$$

Like the methyle-compound, it is readily decomposed by oxide of silver; and the powerfully alkaline solution yields, with hydrochloric acid and bichloride of platinum, a salt of exactly the same appearance as the salt of the methyle-series. This platinum-salt was found to contain

$$C_{36}H_{23}N_2Cl, PtCl_2 = \left.\begin{matrix} C_{16}H_9N \\ C_{16}H_9N \end{matrix}\right\} C_4H_5Cl, PtCl_2.$$

The action of iodide of methyle and ethyle upon ethylene-phenyl-

amine, although different from what might have been anticipated, nevertheless appears to fix in an unequivocal manner the state of substitution of this base. It is obvious that ethylene-phenylamine no longer contains any replaceable hydrogen, and consequently that the molecule $(C_4 H_4)''$, equivalent to H_2 as such, has been assimilated by the aniline.

But how is the composition of the bodies formed by the action of iodide of methyle and ethyle to be interpreted? Are they simply compounds of the alcohol-iodides with 2 equivalents of ethylene-phenylamine, analogous to the salts produced by the union of 1 equiv. iodide of mercury with 2 equivs. of ammonia?

Does not the existence of these bodies involve a further consideration of the formula which has been assigned to ethylene-phenylamine? Does the formula $C_{16} H_9 N$ actually represent the molecule of this body, or is it not more correct to double that expression and to consider the formula $C_{32} H_{18} N_2$ as a more appropriate representation of this molecule? Ethylene-phenylamine would then be derived from 2 equivalents of ammonia, it would be a diamine, and the hydrochlorate and the platinum-compounds would appear in the light of diammonium-compounds.

Diethylene-diphenyl-diamine $\left.\begin{matrix}(C_4 H_4)_2'' \\ (C_{12} H_5)_2\end{matrix}\right\} N_2$.

Bichloride..... $\left.\begin{matrix}(C_4 H_4)'' \\ (C_{12} H_5)_2 \\ H_2\end{matrix}\right\} N_2 Cl_2$.

Platinum-salt..... $\left.\begin{matrix}(C_4 H_4)_2'' \\ (C_{12} H_5)_2 \\ H_2\end{matrix}\right\} N_2 Cl_2, 2PtCl_2$.

At the first glance it certainly appears strange that a molecule capable of assimilating 2 equivs. of hydrochloric acid should unite only with 1 equiv. of iodide of methyle or ethyle, well established members of the hydrochloric type. But this deportment after all is not without parallelism.

The expression

$$C_{20} H_{12} NO_2,$$

originally established for quinine by Liebig, supported as it was by the analysis of numerous salts of the formula

$$C_{20} H_{12} NO_2, HX,$$

and especially by that of a platinum-compound,

$$C_{20} H_{12} NO_2, HCl, PtCl_2, aq,$$

was universally adopted by chemists.

A few quinine-salts of the formula

$$2(C_{20} H_{12} NO_2), HX$$

were considered as anomalous, as basic compounds; and it was not until the methylic and ethylic derivatives of quinine,

$$2C_{20} H_{12} NO_2, C_2 H_3 I \quad \text{and}$$
$$2C_{20} H_{12} NO_2, C_4 H_5 I,$$

had been discovered that chemists began to consider the formula

$$C_{40}H_{24}N_2O_4$$

as a more appropriate expression for the molecule of quinine.

Probably further examination of the salts of ethylene-phenylamine —I retain this name for the present—will furnish saline compounds corresponding to the methyle- and ethyle-derivatives, showing that this base, like quinine, is capable of forming two groups of salts.

It deserves to be noticed that the diammonic nature of ethylene-phenylamine is also strongly marked by its deportment under the influence of heat; for while all the monammonic basic derivatives of aniline are volatile without decomposition, ethylene-phenylamine, when submitted to distillation, is destroyed with reproduction of aniline, like the well-established diamines belonging to this group, melaniline, formyl-diphenylamine, &c.

In describing the preparation of ethylene-phenylamine, it has been mentioned that the action of bibromide of ethylene on aniline gives rise at the same time to two other basic compounds. These substances, which are formed in smaller quantity, differ in a very marked manner from the principal product of the reactions. Their study is not yet completed, but it may even now be stated that they have the same composition as ethylene-phenylamine itself. One of these substances, remarkable for its solubility in spirit, is capable of being converted into ethylene-phenylamine by a simple molecular change. The relation in which these three isomeric bodies stand to each other is not yet finally fixed by experiment. The idea suggests itself that it may possibly be represented by the formulæ—

Soluble base.....	$C_{16}H_9N$.
Ethylene-phenylamine	$C_{32}H_{18}N_2$.
Insoluble base.....	$C_{48}H_{27}N_3$.

"Action of Bichloride of Carbon on Aniline." By A. W. Hofmann, Ph.D., F.R.S.

In two former notes I have described the deportment of aniline as the prototype of primary monamines with the bromine- and chlorine-compounds of biatomic and triatomic radicals. It was found that under the influence of these agents, two equivalents of aniline coalesce to a more complex molecule, retaining the chemical character of the constituents; the action of bibromide of ethylene and chloroform producing respectively—

Diethylene-diphenyl-diamine $C_{32}H_{18}N_2 = \left\{ \begin{matrix} (C_4H_4)_2'' \\ (C_{12}H_5)_2 \end{matrix} \right\} N_2$.

Formyl-diphenyl-diamine .. $C_{26}H_{12}N_2 = \left\{ \begin{matrix} (C_2H)''' \\ (C_{12}H_5)_2 \\ H \end{matrix} \right\} N_2$.

The result of these experiments led me to examine the behaviour of aniline under the influence of organic chlorides containing even a larger number of chlorine equivalents. The agent selected was the body well known by the name of bichloride of carbon, *i. e.* tetra-

chlorinetted marsh-gas, or chloroform, in which the residuary equivalent of hydrogen is replaced by chlorine.

Aniline and bichloride of carbon do not act upon each other at the common temperature; at the temperature of boiling water a change is perceptible, but even after several days' exposure the reaction is far from being complete. On submitting, however, a mixture of $3\frac{1}{2}$ parts by weight of aniline and 1 part of bichloride of carbon, both in the anhydrous state, for about thirty hours to a temperature of 170° C., the liquid will be found to be converted into a black mass, either soft and viscid, or hard and brittle, according to time and temperature.

This black mass, which adheres firmly to the tubes in which the reaction has been accomplished, is a mixture of several bodies. On exhausting with water, a portion dissolves, while a more or less solid resin remains behind.

The aqueous solution yields, on addition of potassa, an oily precipitate containing a considerable portion of unchanged aniline; on boiling this precipitate with dilute potassa in a retort, the aniline distils over, whilst a viscid oil remains behind, which gradually solidifies with a crystalline structure. Washing with cold alcohol and two or three crystallizations from boiling alcohol render this body perfectly white and pure, a very soluble substance of a magnificent crimson colour remaining in solution.

The portion of the black mass which is insoluble in water dissolves almost entirely in dilute hydrochloric acid, from which solution it is reprecipitated by the alkalies in the form of an amorphous pink or dingy precipitate soluble in alcohol with a rich crimson colour. The greater portion of this body consists of the same colouring principle which accompanies the white crystalline substance. On the other hand, considerable quantities of this crystalline body are occasionally present in the product insoluble in water.

The crystalline body is insoluble in water, difficultly soluble in boiling alcohol, soluble in ether. From the hot alcoholic solution it crystallizes slowly on cooling in elongated four-sided plates, often grouped round a common centre; this substance is a well defined base; it freely dissolves in acids, from which, on the addition of the alkalies, it is thrown down as a dazzling white precipitate.

The analysis of this new base has led to the expression

$$C_{38}\,H_{17}\,N_3,$$

a formula corroborated by the analysis of a fine, somewhat difficultly soluble hydrochlorate,

$$C_{38}\,H_{17}\,N_3,\,HCl,$$

which is obtained by dissolving an excess of the new base in hot diluted hydrochloric acid, when it crystallizes on cooling.

A further confirmation was furnished by the examination of a bright yellow platinum-salt,

$$C_{38}\,H_{17}\,N_3,\,HCl,\,PtCl_2.$$

Both the hydrochlorate and the platinum-salt are extremely soluble

in an excess of hydrochloric acid, which has therefore to be carefully avoided in their preparation.

The phase of the action of bichloride of carbon on aniline, which gives rise to the formation of the new base, is expressed by the equation

$$6C_{12}H_7N + C_2Cl_4 = C_{38}H_{17}N_3, HCl + 3(C_{12}H_7N, HCl).$$

What is the constitution of the new body? It is obviously derived from 3 molecules of aniline from which 4 equivalents of hydrogen have been eliminated by the 4 equivalents of chlorine in the bichloride, the carbon entering as a biatomic molecule into the complex atom. The new body would thus become a triamine,

$$\left.\begin{matrix} C_2'' \\ (C_{12}H_5)_3 \\ H_2 \end{matrix}\right\} N_3.$$

It is however more probable that the carbon replaces in the form of cyanogen, when the new compound appears in the light of a diamine, as

$$\text{Cyan-triphenyl-diamine } \left.\begin{matrix} C_2N \\ (C_{12}H_5)_3 \\ H_2 \end{matrix}\right\} N_2.$$

The new compound thus becomes closely allied to melaniline, which may be viewed as diphenyl-cyan-diamine,

$$\text{Melaniline } C_{26}H_{13}N_3 = \left.\begin{matrix} C_2N \\ (C_{12}H_5)_2 \\ H_3 \end{matrix}\right\} N_2.$$

It deserves to be noticed, that in its appearance, and in its general characters, cyan-triphenyl-diamine resembles melaniline in a remarkable manner.

If we are entitled to view the new body which forms the subject of this note as a cyanogen-substitute, we have not less than four well-defined diamines of the phenyle-series.

$$\text{Diethylene-diphenyl-diamine } \left.\begin{matrix} (C_4H_4)''_2 \\ (C_{12}H_5)_2 \end{matrix}\right\} N_2.$$

$$\text{Formyl-diphenyl-diamine .... } \left.\begin{matrix} (C_2H)''' \\ (C_{12}H_5)_2 \\ H \end{matrix}\right\} N_2.$$

$$\text{Cyan-diphenyl-diamine ..... } \left.\begin{matrix} C_2N \\ (C_{12}H_5)_2 \\ H_3 \end{matrix}\right\} N_2.$$

$$\text{Cyan-triphenyl-diamine..... } \left.\begin{matrix} C_2N \\ (C_{12}H_5)_3 \\ H_2 \end{matrix}\right\} N_2.$$

I intend to continue the inquiry still further in this direction, and propose next to examine the deportment of aniline with the so-called protochloride (C_4Cl_4) and sesquichloride of carbon (C_4Cl_6).

THE CHEMICAL GAZETTE.

No. CCCLXXXIV.—October 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Pyrogallic Acid. *By* A. ROSING.

ALTHOUGH the quantitative relation of the elements in pyrogallic acid has been long since accurately fixed, its equivalent has not yet been determined satisfactorily. Different chemists have attributed to this body the formulæ

$$C^8 H^4 O^4,\ C^6 H^3 O^3,\ \text{and}\ C^{12} H^6 O^6,$$

all of which, however, have been deduced from a single compound, that formed by pyrogallic acid with oxide of lead, and obtained by precipitating neutral acetate of lead by a solution of pyrogallic acid. The lead-salt has been employed, notwithstanding the inconveniences attending its use, because no other means could be had recourse to, as pyrogallic acid does not combine with ammonia or the other alkalies, and the compounds which it forms with the other metallic oxides are even less stable than the lead-salt. In preparing the latter the author found that even when it was obtained perfectly white by washing the precipitate without access of air, with water slightly acidulated with acetic acid, its composition was extremely variable.

In attempting to form compounds of greater stability, the author tried the oxides with less prominent basic properties. Braconnot mentions a compound of pyrogallic acid with alumina, stating that he obtained it by dissolving freshly precipitated hydrate of alumina in an aqueous solution of pyrogallic acid. The author thinks that this is not a true chemical combination, but a simple solution with oxidation of the acid, as the liquid becomes considerably coloured; far from furnishing crystals as described by Braconnot, the liquid leaves a resinous mass on evaporation. Oxide of chrome and the peroxides of iron and uranium furnished no better results; they behave like alumina.

The author found that oxide of antimony furnished a well-defined compound with pyrogallic acid. To prepare this compound, a tolerably concentrated solution of pyrogallic acid is poured into a boiling solution of tartrate of potash and antimony, when fine, white, crystalline lamina of a pearly lustre are soon precipitated.

The precipitate is allowed to collect, and the liquid, which furnishes crystals of bitartrate of potash on cooling, is decanted; the precipitate is washed with boiling water on a filter, and finally dried at 212° F. The crystals thus prepared are reduced to a powder by friction between the fingers, and produce the same sensation as talc; they are perfectly unalterable in the air, even when heated to 257° F. They are insoluble in water and the other ordinary solvents, but dissolve readily in weak muriatic acid. Nitric acid produces the same reaction upon this body as upon pyrogallic acid.

If the solutions be mixed cold, the precipitate is not formed for some time, and well-defined crystals are not obtained in this case.

The analysis of this compound gave the following numbers, the antimony being determined in the form of sulphuret:—

	I.	II.	III.	IV.
C	27·26	27·59	27·75	27·88
H	2·09	2·18	2·20	2·19
Sb	46·70	..	46·52	
O				

The analyses I. and II. were effected with the same, the others with different samples.

These results agree with the formula $C^{12} H^5 Sb O^6$, which requires C=27·37, H=1·90, Sb=46·38, so that this body may be regarded as a pyrogallate of antimonyle:—

$$C^{12} \left\{ \begin{matrix} H^5 \\ SbO^2 \end{matrix} \right. O^6,$$

and from this it is no longer doubtful that the equivalent of pyrogallic acid must be expressed by the formula

$$C^{12} H^6 O^6.$$

In his former memoir the author mentioned that pyrogallic acid dissolves in monohydrated sulphuric acid. The solution is of a slightly yellow colour and perfectly limpid; after some time it sets into a white mass, which becomes liquified again, if it be pressed between two porous tiles to free it from the excess of sulphuric acid. If, after dissolving the substance in water and saturating the sulphuric acid by carbonate of baryta, the whole be placed upon a filter, the filtrate appears to contain a baryta-salt of a sulpho-conjugate body, but this is decomposed by evaporation even when the air is excluded.

When pyrogallic acid is mixed with concentrated potash, and the whole is boiled until the liquid becomes syrupous, it sets on cooling into a black, crystalline mass. On adding sulphuric acid, much carbonic acid is evolved, and by distillation a product is obtained in which the presence of acetic acid is easily ascertained. If another portion of the black mass be dissolved in water and acetic acid be added in excess, solution of chloride of calcium furnishes a precipitate of oxalate of lime. The decomposition of pyrogallic acid may therefore be expressed by the following equation:—

$$C^{12} H^6 O^6 + 14O = C^4 H^2 O^8 + C^4 H^4 O^4 + 4CO^2.$$

In his former memoir the author has shown that when, under the

influence of ammonia and the air, pyrogallic acid acquires the well-known brown colour, a nitrogenous, neutral, and uncrystallizable body is formed, for which he has proposed the name of *pyrogalleine* He did not then venture to give a formula for this body, as the analyses of different preparations were rather discordant, and this appears to be due to variations in the duration of the action of the ammonia. He has since prepared pyrogalleine in the following manner:—the acid is dissolved in aqueous ammonia, and the solution exposed for a fortnight to the action of the air in plates, in order to get the largest possible surface of liquid. Ammonia is added from time to time. Lastly, a current of oxygen is passed through the liquid for some hours, and it is then evaporated to dryness in the water-bath; the brown mass is dried for several days at 212° F., until it loses nothing in weight. This appears to be the final product of the reaction, for when moistened again with ammonia and exposed to the air, it did not change in composition. Its analysis gave,—

	I.	II.
C	44·86	44·74
H	4·28	4·12
N	17·42	17·88
O		

This corresponds with the formulæ

$$C^{18}H^{10}N^{3}O^{10}, \text{ or } C^{36}H^{20}N^{6}O^{20},$$

which require

$$C=45{\cdot}00,\ H=4{\cdot}16,\ N=17{\cdot}50,\ O=33{\cdot}33.$$

The constitution of this compound must be determined by further investigations. Its mode of formation may be explained by the equation:—

$$3(C^{12}H^{6}O^{6})+6NH^{3}+18O=16HO+C^{36}H^{20}N^{6}O^{20}.$$

This equation is analogous to that which shows the mode of formation of orceine:—

$$C^{14}H^{6}O^{4}+NH^{3}+4O=2HO+C^{14}H^{7}NO^{6}.$$

Pyrogalleine gives brown precipitates with a great number of metallic salts, but these precipitates cannot be washed without undergoing decomposition.—*Comptes Rendus*, June 14, 1858, p. 1139.

On some new Æthers of Stearic and Margaric Acids.
By M. HANHART.

The comparative study of various æthers has led to the establishment of a number of general relations between the physical properties of these bodies and their chemical composition. To indicate all the interest attached to researches of this kind, it is sufficient to refer to the relations which exist between the densities, points of ebullition, specific heats, and indices of refraction of compound æthers and the same properties, viewed in their generators, that is to say, in the acids and alcohols.

It has occurred to me that it might be interesting in this point of

view to compare one of the most delicate of the physical properties, the melting-point in compounds very analogous to each other in their most essential physical and chemical properties; I allude to the æthers formed by the union of fatty acids with different alcohols. I have employed on the one hand stearic and margaric acids, on the other ordinary methylic, amylic, and caprylic alcohols. The employment of perfectly pure fatty acids was essential in the present researches, for the slightest intermixture would have destroyed all the value of the results. The stearic acid was extracted from mutton suet by M. Chevreul's method, it was fusible at 158° F.; the margaric acid was extracted from human fat, it fused at 140° F.

With regard to the fatty æthers themselves, I prepared them generally by M. Berthelot's method*, by heating the alcohol and the acid for a day at 392° F. in a tube hermetically sealed; the product was mixed with a little æther, and it was digested some time with slaked lime in the water-bath, to separate the free acid from the neutral compound. It was taken up again with common æther. If the alcohol employed is not very volatile, its excess may be eliminated by the use of common alcohol, in which the fatty æthers are but very slightly soluble. The compound should be neutral to tincture of litmus dissolved in boiling alcohol. The fatty æthers may also be prepared by the ordinary process, by causing a current of dry hydrochloric acid gas to pass for three hours through a mixture of the respective alcohol and the acid. But this method does not furnish such pure fatty æthers as the preceding.

I have studied the following æthers:—methylo-margaric, ethylo-margaric, amylo-margaric, caprylo-margaric, methylo-stearic, ethylo-stearic, amylo-stearic, and caprylo-stearic. Among these substances the amylo-margaric, caprylo-margaric, and caprylo-stearic are new. These three æthers are neutral, liquid at ordinary temperatures; they are colourless, inodorous, insipid, and stain paper like liquid fatty matters. The formulæ of these three substances are not doubtful, but for the sake of greater certainty I have analysed amylo-margaric æther,—

$$C^{44}\,H^{44}\,O^{4} = C^{34}\,H^{34}\,O^{4} + C^{10}\,H^{12}\,O^{2} - 2\,HO.$$

	Calculated.	Found.
Carbon....	77·65	77·43
Hydrogen..	12·95	13·13
Oxygen....	9·40	9·44

The following are the melting-points of these different æthers:—

	Margaric æthers.	Stearic æthers.	Difference.
Methylic.....	80°·5	100°·4	19°·9
Ethylic	71·6	87·8	16·2
Amylic	57·2†	36·5	20·7
Caprylic	47·3	23·9	23·4
Margaric acid....	140	Stearic acid 158	18·0

* Ann. de Chimie et de Physique, 3 sér. xli. p. 440 (1854).

† Solidifies at 51°·8.

These melting-points may be compared under two distinct points of view.

1. If we compare each margaric æther with the corresponding stearic æther, we observe that the stearic æther generally melts at a higher temperature than the corresponding margaric æther. The difference is from 16° to 20° F., that is to say, pretty nearly the same as that which exists between the pure fatty acids. But the caprylic æthers form an exception, perhaps on account of some impurity. In the other cases, we find the same approximative proportionality which is generally observed between the variation of the physical property and the variation of the chemical equivalent of analogous compounds.

2. But the comparison of the melting-points of the æthers formed by the same acid with the different alcohols, presents a very singular peculiarity: in proportion as the equivalent of the alcohol rises, the melting-point of the fatty æther falls, and this declension does not appear to follow even approximatively a regular proportion. Moreover, it does not appear to continue to the end of the series of alcohols, for the margaric æthers of ethalic, cerotic, and melissic alcohols appear to have their boiling-points much more elevated than any of the preceding, at least so far as can be judged from spermaceti, china-wax, and bees'-wax. If therefore we seek to represent by a curve the sequence of the melting-points, the equivalent being taken for the abscissa and the temperature of fusion for the ordinate, this curve, after having approached the axis of the abscissæ by continually descending, will subsequently change its direction, and on rising depart from it.

It is difficult to explain the real causes of this phænomenon, but it appears to be connected with the hitherto unknown melting-points of the various alcohols, and with their physical condition more and more removed from that of water and approaching to that of fatty bodies.

Indeed, we cannot avoid bringing together the melting-points presented by the fatty æthers of the various alcohols and those of the acids corresponding to the same alcohols: formic acid and acetic acid, fluid like water, miscible with that liquid, are fusible at ordinary temperatures, while butyric and valeric, already oily and little soluble in water, only solidify at a temperature far below 32°. On the contrary, the melting-points of the fatty acids, properly so called, rise to 158°, 176°, and higher.

Thus the course of the melting-points of the acids is analogous to that of the melting-points of the æthers formed by any one fatty acid with the different alcohols corresponding to the same acids.—*Comptes Rendus*, August 2, 1858, p. 230.

Note on the Equivalent of Aluminium. *By* C. Tissier.

Having remarked that in different reactions the number 14, adopted by many chemists as the equivalent of aluminium in rela-

tion to hydrogen, appeared to be too high, I have endeavoured to determine directly whether this number was really correct.

With this view I have laboured to obtain aluminium as pure as possible by reducing perfectly pure fluoride of aluminium and sodium, by sodium previously purified. The reduction was effected in a charcoal crucible, and the metal was fused several times to free it from small quantities of the flux which it might have retained.

Analysis of the Aluminium thus obtained.

Testing for Iron.—The metal was dissolved in nitromuriatic acid; the liquid, evaporated to dryness with a great excess of nitric acid, left, after calcination, alumina of a dazzling whiteness. The addition of a liquid containing a few thousandths of iron was sufficient to give it a very strong red colour.

Testing for Silicium.—The metal when dissolved in muriatic acid, left no trace of silicium.

Testing for Sodium.—1 grm. of the alumina obtained by the evaporation of the product of the action of nitric and nitromuriatic acids was digested with a boiling concentrated solution of nitrate of ammonia. The liquid when evaporated gave,—dry residue 0·005 grm. This residue consisted of nitrate of soda, which gives for the quantity of sodium contained in the metal 0·00135 grm., or a little more than one-thousandth.

Determination of the Equivalent.—1·935 grm. of metal was dissolved in muriatic acid; the solution was evaporated with an excess of nitric acid until all the chlorine was completely expelled, and the product of the evaporation heated sufficiently to drive off all the nitric acid.

Weight of alumina obtained.....	3·645 grm.
Weight of alumina calculated, assuming 13·75 for the equivalent of aluminium	3·625 „
Weight of alumina calculated, assuming 14 for the equivalent of aluminium	3·590 „

I think from this that the equivalent of aluminium should be below 14. I should not have thought of publishing these results, if I had not had the pleasure of seeing them confirmed by the number which M. Dumas assigns to the equivalent of aluminium, considering it as a multiple of one-fourth of the weight of hydrogen. In fact, if we multiply 0·25 by 55 we get 13·75, which appears in all probability to be the exact number.—*Comptes Rendus*, June 7, 1858, p. 1105.

Investigation of Strychnine. By P. Schutzenberger.

When a mixture of sulphate of strychnine and nitrite of potash dissolved in water is boiled, a brisk effervescence due to the liberation of nitrogen gas is observed. After the reaction the yellowish liquid treated with ammonia furnishes a light yellow, flocculent precipitate.

The washed precipitate is dissolved in boiling alcohol. On cool-

ing, the liquid deposits transparent, well-defined crystals of considerable size and of a fine orange-yellow colour; they appear to be right prisms with a rectangular base, and with truncations at the solid angles. The supernatant alcohol, when concentrated, furnishes a fresh deposit of separate prisms of a darker orange-red colour.

These two bodies form two new alkaloids, and represent two degrees of oxidation of strychnine.

The red base is more oxidized than the orange one. They are both insoluble in water, soluble in alcohol (the red one more than the other), and insoluble in æther. They contain no water of crystallization, are decomposed at about 572° F., fuse on a plate of platinum, and burn with a brilliant flame. Their taste is bitter, but less so than that of strychnine.

The orange base dried at 482° F., loses nothing at a higher temperature, and gave on analysis,—

C	62·5
H	7·06

It also gave 7·05 per cent. of nitrogen, leading to the formula

$$C^{42}H^{28}N^{2}O^{12} = \underbrace{C^{42}H^{22}N^{2}O^{4}}_{\text{Strychnine.}} + 6HO + O^{2}.$$

Theory,—

C	62·37
H	6·93
N	6·93

The chloroplatinate gave 16·10 per cent. of platinum; the formula $C^{42}H^{28}N^{19}O^{2}Cl\,HCl^{2}Pt$ requires 16·2 per cent. This base may be called *oxystrychnine*.

The red base gave—

		Calculated.
C	59·76	60·00
H	6·85	6·6
N	6·52	6 6

leading to the formula

$$C^{42}H^{28}N^{2}O^{14} = C^{42}H^{22}N^{2}O^{4} + 6HO + O^{4}.$$

The chloroplatinate gave 15·65 per cent. of platinum; calculated 15·8 per cent. This alkaloid contains 2 equivs. of oxygen more than the preceding, and may be named *binoxystrychnine*.

From numerous analyses of strychnine, the author concludes that this body is not constant in its composition. His analyses, and those of Regnault made with octahedric strychnine, agree with the formula

$$C^{40}H^{22}N^{2}O^{4}.$$

The most common strychnine, from numerous analyses, has the formula adopted, namely,—

$$C^{42}H^{22}N^{2}O^{4}.$$

Lastly, Gerhardt has published several analyses of chloroplatinate of strychnine, in which the carbon is 1 per cent. too high and the nitrogen 0·5 per cent. too low for the admitted formula, but which agree perfectly with

$$C^{44}H^{22}N^{2}O^{4}.$$

This is rendered more probable by the fact of the same thing taking place with other bases.—*Comptes Rendus*, July 12, 1858, p. 79.

On Melezitose, a new kind of Sugar. *By* M. BERTHELOT.

In continuing the study of the saccharine matters some years ago, I found in the manna of Briançon, a saccharine exudation produced by the larch, and formerly used in medicine, a new sugar analogous to cane-sugar, but I was unable to complete the study of it for want of material. Having subsequently succeeded in obtaining a sufficient quantity of this manna, thanks to M. Meissas, I again took up the subject, and have succeeded in isolating and characterizing the sugar it contained; it is a new substance, very interesting from its analogy to cane-sugar; I shall call it *melezitose*.

In order to extract it, the manna of Briançon is treated with boiling alcohol, which is evaporated to the consistence of an extract and left for some weeks. The melezitose crystallized in a syrupy mother-liquor; it was pressed, washed with warm alcohol, and recrystallized from boiling alcohol; in this way it was obtained in very small, hard and shining crystals; examined with the microscope, they appeared to be oblique rhomboidal prisms, analogous to those of cane-sugar. I could not obtain them of sufficient size to admit of measuring their angles. Seen in mass, the crystals present an opake appearance which does not present itself in single crystals. Their taste is sweet, analogous to that of glucose, and consequently much weaker than that of cane-sugar. They are very soluble in water, almost insoluble in cold alcohol, slightly soluble in boiling ordinary alcohol. Absolute alcohol added to a concentrated aqueous solution of melezitose precipitates it slowly in a crystalline form; its aqueous solution left to evaporate spontaneously becomes syrupy, and remains long without crystallizing.

Melezitose, dried at 230° F., presents the same composition as cane-sugar, and corresponds to the formula $C^{12} H^{11} O^{11}$. Below 284° F. it fuses into a transparent liquid without sensible alteration. Its reactions are similar to those of cane-sugar. It does not sensibly reduce the tartrate of potash and copper, and is not destroyed by alkalies at 212° F., but cold concentrated sulphuric acid carbonizes it, and it turns brown rapidly under the influence of boiling hydrochloric acid. Dilute sulphuric acid changes it at 212° F. into a sugar analogous or identical with glucose, capable of reducing tartrate of potash and copper, and destructible by alkalies at 212° F. Nitric acid converts it into oxalic acid, without any mucic acid. Ammoniacal acetate of lead precipitates it. Melezitose treated with yeast ferments only slowly and incompletely, sometimes not at all; but if it has been modified by sulphuric acid, it ferments immediately, changing almost entirely into alcohol and carbonic acid.

Its rotating power at 58° F., deduced from a solution at $\frac{1}{5}$th, and referred to the tint of passage, equals +90°·3 A solution containing $\frac{1}{100}$th of sulphuric acid deviated +17°·7; heated to 212° F.

for ten minutes, $+12°{\cdot}2$; for one hour, $=9°{\cdot}8$; for two hours, $+9°{\cdot}8$.

Thus the rotating power of melezitose is $\frac{1}{4}$th higher than that of cane-sugar; under the influence of sulphuric acid, it diminishes more slowly than that of cane-sugar, and does not change its sign, while that of cane-sugar is reversed; this remark is essential. The rotating power of the modified melezitose is almost identical with that of glucose.

These characters, conjoined with the less sweet taste and the much more difficult fermentation, distinguish melezitose from cane-sugar.

Trehalose is distinguished from melezitose by its rotating power equal to $+208°$, and by a notably greater stability.

With regard to melitose, it possesses a rotating power scarcely different from that of melezitose, and varying in like manner under the influence of sulphuric acid. But melitose ferments more readily and with a special character, for it only ferments to the extent of one-half; moreover it furnishes mucic acid.

From these facts it is evident that cane-sugar, long isolated by its characters, becomes the type of a class of saccharine bodies which is constantly increasing in number. The same remark will apply to grape-sugar.

The term glucose, indeed, hitherto applied to grape-sugar alone, now denotes a series of distinct saccharine principles, such as the glucose of grapes, glucose of malt, glucose of fruits, glucose of lignose, lactic glucose, and perhaps glucose of gum, &c.; all these glucoses are saccharine bodies, directly fermentable, alterable by alkalies, reducing tartrate of potash and copper, &c. In like manner there have come to group themselves beside cane-sugar, different sugars difficult of fermentation, not alterable at 212° F. by alkalies and tartrate of potash and copper, represented at 266° F. by the formula $C^{12}H^{11}O^{11}$, modified by acids, and capable of conversion into new sugars belonging to the class of the glucoses.

Some years ago I discovered the first example of this new series of sugar, analogous to cane-sugar, melitose; last year I published a second example, trehalose. The mycose of Mitscherlich, discovered since, and melezitose are to be added to the number of sugars belonging to this group.

It will be essential henceforth to take these results into account in analytic researches relating to the study of saccharine matters, and no longer to confound with cane-sugar the analogous sugars, as has doubtless been done more than once, through depending solely upon the general reactions presented by their solutions, and neglecting to obtain the sugars themselves in a pure isolated condition.

These results are no less worthy of attention in a synthetic point of view; they prove that the artificial formation of cane-sugar is a problem far more complicated than was at first supposed while no isomeric sugar was known. In fact, the processes by which such a sugar may be produced, at least, if not discovered by accident, must

depend upon a comparative study of the different isomeric principles, and furnish the general law of their formation.—*Comptes Rendus*, August 2, 1858.

On some Compounds of Chromic Acid with Oxide of Mercury. *By* A. Geuther.

Neutral Chromate of Mercury, HgO, CrO^3, is obtained when about equal quantities of pure dry chromic acid (in a moderately concentrated solution) and yellow oxide of mercury are boiled together and gradually evaporated until all the yellow oxide has disappeared, and red crystals have made their appearance in its place.

They are deep garnet-red rhombic prisms, which are converted by water even at ordinary temperatures, but completely when heated, into the amorphous compound $(HgO)^3 + CrO^3$ and free chromic acid. The crystals dissolve readily in muriatic acid, and solution of soda precipitates yellow oxide of mercury from this solution. Concentrated nitric acid in the cold converts it into an amorphous yellow compound, whilst a great portion is dissolved. Moderately concentrated nitric acid and dilute sulphuric acid have the same action, except that a larger quantity of the yellow compound is left. The latter, and the yellow compound produced by the action of solution of soda upon the crystals, appear to be identical with the following compound.

Basic Chromate of Mercury, $(HgO)^7 + 2\,CrO^3$, is produced, when the greatly diluted mother-liquor of the preceding salt is precipitated by carbonate of soda, and the precipitate is boiled with solution of soda. The precipitate thrown down by carbonate of soda contains $(HgO)^5\,CrO^3$, together with a compound containing more chromic acid. By boiling with solution of soda there is then produced—

$$2\big((HgO)^5, CrO^3 + HgO\,CrO^3\big) + 2\,NaO = (HgO)^7 + 2\,CrO^3 + HgO + 2\,NaO\,CrO^3.$$

It is also formed when freshly precipitated oxide of mercury is boiled for a long time with a concentrated solution of bichromate of potash, until it is converted into a tile-red powder, with formation of neutral chromate of potash, and this powder is heated, after washing, with moderately concentrated nitric acid. A portion is dissolved whilst the yellow compound remains.

This salt is an amorphous, heavy, yellow powder, with a tinge of orange, which dissolves rapidly in nitric acid only when it is freshly precipitated, and has not been boiled (with solution of soda). It is converted into white sulphate of mercury only by concentrated sulphuric acid, and by this only when boiled; muriatic acid dissolves it readily.—Liebig's *Annalen*, cvi. p. 244.

On the Double Acetates of Uranium. *By* P. Weselsky.

The following communication contains the results of the investigation of some double acetates of uranium, belonging to the series of those first prepared by J. Wertheim.

They were prepared by mixing the corresponding simple salts in equivalent proportions, and the crystals obtained were subsequently crystallized repeatedly with the addition of free acetic acid. The investigation was effected partly by the method of H. Rose and partly by the method proposed by W. Knop, for the determination of phosphoric acid, which the author reversed and applied to oxide of uranium. The former consists in treating the solution of the salt with an excess of carbonate of baryta, and stirring it frequently at the ordinary temperature. After the complete precipitation of the oxide of uranium, which takes place in about 24 hours, it is separated by filtration together with the undecomposed carbonate of baryta, washed, and dissolved in muriatic acid; the baryta is precipitated by sulphuric acid, and the uranium is thrown down by caustic ammonia from the fluid filtered from the sulphate of baryta which is first heated to boiling, and the precipitate is calcined and weighed as protoperoxide of uranium.

The oxides not thrown down by carbonate of baryta were determined by the ordinary methods from the filtrate from the oxide of uranium and baryta, after the solution had been freed from baryta by means of sulphuric acid.

In the method described by Knop for the determination of phosphoric acid, caustic ammonia is added to the substance containing phosphoric acid, which has previously been dissolved in muriatic or nitric acid; it is then heated with acetic acid, and lastly acetate of uranium is added. In this way a precipitate of phosphate of uranium and ammonia is obtained, which, when calcined, is $2U^2O^3$, PO^5, and is weighed in this form. In his determinations the author mixed the double salt with caustic ammonia, dissolved the oxide of uranium and ammonia formed in free acetic acid, and added ordinary phosphate of soda.

The salts investigated by the author are all constituted in accordance with the type $RO,C^4H^3O^3, 2U^2O^3C^4H^3O^3, nHO$, with the exception of the cadmium-salt, which agrees with the formula $CdO\,C^4H^3O^3, U^2O^3C^4H^3O^3$, and is therefore analogous to the lead-salt described by J. Wertheim. They retain the yellow colour of acetate of uranium when the other simple salt is colourless, and are changed in colour when the latter is coloured. They are all readily soluble in water. The measurements of the crystals were performed by Professor Grailich.

$NiO, 2U^2O^3, 3C^4H^3O^3, 7HO$.—This salt crystallizes in the orthotypic system, $a:b:c = 1:0{\cdot}8977:0{\cdot}9140$; it possesses an emerald-green colour, and loses no water either in the air or *in vacuo* over sulphuric acid. At 212° F. it becomes yellowish, but only loses all its water of crystallization at 356° F. Analysis:—

U^2O^3	52·66	52·05	52·53	53·043	2=288		53·175
NiO	..	..	..	..	1	37·6	6·943
$C^4H^3O^3$	..	..	..	..	3	153	28·249
HO	..	..	11·71	11·492	7	63	11·633

$CoO, 2U^2O^3, 3C^4H^3O^3, 7HO$.—This salt possesses the same

crystalline form as the nickel-salt; it has a greenish-brown colour and resembles the preceding compound in its other properties, except that its colour becomes darker at 212° F., and grayish-violet at 356° F. Analysis:—

U^2O^3	52·701	52·587	53·788	..	2	288	53·185
CoO	..	6·404	..	..	1	37·5	6·925
$C^4H^3O^3$	..	..	..	..	3	153	28·254
HO	..	11·706	..	12·069	7	63	11·636

ZnO, $2U^2O^3$, $3C^4H^3O^3$, 7HO.—It possesses a sulphur-yellow colour, crystallizes like the preceding salts, and behaves to water and air, and also on exposure to high temperatures, like the nickel- and cobalt-salts; at 365° F. the colour becomes dingy gray. Analysis:—

U^2O^3	53·2	52·24	2	288	52·882
ZnO	..	6·245	1	40·6	7·45
$C^4H^3O^3$	..	..	3	153	28·094
HO	..	11·446	7	63	11·566

MgO, $2U^2O^3$, $3C^4H^3O^3$, 12HO.—This compound crystallizes in the orthotypic system, $a:b:c=1:0{\cdot}6042:0{\cdot}3960$, and exhibits a dichroism in a far higher degree than nitrate of uranium; it forms up to a temperature of 64°·4 F., effloresces in the air with great ease, loses 6 equivs. of water over sulphuric acid, and becomes converted into the salt described by Rammelsberg; at 392° F. it loses all its water of crystallization. Analysis:—

U^2O^3	50·72	2	288	50·615
MgO	3·71	1	20	3·515
$C^4H^3O^3$	..	3	153	26·889
HO	19·18	12	108	18·981

MnO, $2U^2O^3$, $3C^4H^3O^3$, 12HO.—This salt crystallizes like the magnesia-salt, possesses a yellow colour, and also effloresces with great facility; at 392° F. it loses all its water. Analysis:—

U^2O^3	48·79	48·41	2	288	49·28
MnO	..	5·881	1	35·6	6·08
$C^4H^3O^3$	..	..	3	153	26·17
HO	18·15	..	12	108	18·47

CaO, $2U^2O^3$, $3C^4H^3O^3$, 8HO.—In his memoir upon uranium Wertheim mentions this as well as the following salt, but without having investigated them.

The lime-salt possesses a sulphur-yellow colour, crystallizes in the orthotypic system, $a:b:c=1:0{\cdot}9798:0{\cdot}389$; it is stable in the air, and only loses the whole of its water of crystallization at 392° F. Analysis:—

U^2O^3	..	53·73	52·83	2	288	53·234
CaO	5·57	5·346	..	1	28	5·175
$C^4H^3O^3$	..	..	..	3	153	28·281
HO	12·611	..	..	8	72	13·310

SrO, $2U^2O^3$, $3C^4H^3O^3$, 6HO.—This salt crystallizes in the pyramidal system, character of the combination hemipyramidal with

inclined faces $a=3°63$; it possesses the same colour and properties as the lime-salt. Analysis:—

U^2O^3	53·08	52·76	..	2	288	52·670
SrO	8·89	..	..	1	51·8	9·470
$C^4H^3O^3$	..	..	..	3	153	27·986
HO	..	..	10·06	6	54	9·874

CdO, U^2O^3, $2C^4H^3O^3$, 5 HO.—The crystalline form is the same as that of the magnesia-salt, and it exhibits the same dichroism; it only becomes slightly opake by long exposure to the air, fuses at 212° F., and loses all its water at 356° F.

For the investigation of this salt the solution was strongly acidified with muriatic acid, and the cadmium was then precipitated by sulphuretted hydrogen. The sulphuret of cadmium formed was separated by filtration, oxidized by nitric acid, precipitated by carbonate of soda and determined as oxide of cadmium; the excess of sulphuretted hydrogen was driven off from the filtrate by heat, and the uranium obtained in the usual way by precipitation with caustic ammonia. Analysis:—

U^2O^3	40·10	40·62	..	40·9	1=144	40·563
CdO	..	18·1	..	..	1 64	18·029
$C^4H^3O^3$	..	..	..	..	2 102	28·733
HO	..	13·56	13·3	..	5 45	12·676

Sitzungsber. der Akad. der Wiss. zu Wien, xxx. p. 205.

ANALYTICAL CHEMISTRY.

On the Employment of Permanganate of Potash as an agent of Oxidation, for the determination of Sulphur in Gunpowder and Sulphuretted Compounds in general. *By* S. Cloëz *and* E. Guignet.

To determine the sulphur contained in a sulphuretted material, the most exact process consists in converting the sulphur into sulphuric acid, which is then precipitated by a soluble salt of baryta. Nitric acid is usually employed for the oxidation of the sulphur, but its action is slow and difficult. It only becomes complete by long boiling with concentrated nitric acid, and in operating upon sulphuretted organic matters, we have to fear either an imperfect oxidation or a loss of sulphuric acid by volatilization. The action of nitric acid is therefore often replaced by that of a mixture of nitrate of potash and an alkaline carbonate in fusion, into which the matter to be analysed is thrown in small portions. This process is inconvenient in operating upon gunpowder, which must be mixed with several times its weight of chloride of sodium, in order to moderate the reaction.

The authors propose to effect the conversion of sulphur into sulphuric acid by means of permanganate of potash. For this purpose crystallized permanganate, containing no appreciable traces of sulphate, must be employed. To ascertain that the salt contains no sulphate of potash, a small quantity may be boiled with pure

muriatic acid until it is completely decomposed; the liquid should not precipitate chloride of barium.

The operation is performed as follows, taking gunpowder as an example of the material to be analysed:—About 1 grm. of powder is weighed very accurately, and dried in a stove or a current of dry air at 212° F. until it no longer loses in weight; in this way the quantity of water is determined. The dried material is then put into a small glass matrass with a saturated solution of permanganate of potash; and the liquid is boiled, with the addition of permanganate from time to time, until the mixture has a persistent violet tint.

All the sulphur in the powder is then converted into sulphuric acid, and the carbon into carbonic acid; the liquid holds oxide of manganese in suspension; concentrated muriatic acid is added, and the whole is boiled until the oxide is completely dissolved, which only requires a few minutes. If the solution of the oxide be slow, the liquid is too dilute, and must be concentrated by evaporation; after which pure muriatic acid is again added; a slight excess of chloride of barium is then poured into the balloon, so as to precipitate all the sulphuric acid, a little nitric acid is added, and the whole is boiled so as to give coherence to the precipitate of sulphate of baryta. The latter is then washed with distilled water on the filter until the washing-water produces no turbidity in nitrate of silver. The filter is calcined with its contents in a platinum capsule, and weighed, deducting the weight of the ashes of the filter in the ordinary way.

In a laboratory where numerous determinations of sulphur have to be made daily, instead of collecting and weighing the sulphate of baryta, the liquid might be precipitated by a normal solution of chloride of barium by the *method of successive approximations*. The results are very exact, and the whole operation does not last more than a quarter of an hour.

The finely divided carbon contained in powder being readily and completely oxidized by permanganate of potash, the authors think it possible that this reagent may be applied to the determination of the carbon contained in animal charcoal, or in other matters containing finely divided carbon.

The analysis of the saline compounds of sulphur is very easily effected by permanganate of potash. Hyposulphite of soda reduces the solution of permanganate immediately in the cold, and by adopting the same course as with gunpowder, the authors obtained the following results:—1·000 gr. of commercial crystallized hyposulphite of soda gave 1·850 gr. of sulphate of baryta, containing 0·254 gr. of sulphur. Calculation from the formula S^2O^2, NaO, 5HO requires 0·258 gr.

The authors have ascertained that this method does not apply only to bodies which attract oxygen with avidity, but that the most stable sulphuretted compounds are completely oxidized by permanganate of potash, the sulphur being entirely converted into sulphuric acid; thus sulphuret of carbon, which resists ebullition with fuming nitric acid, and dissolves hyponitric acid without being

decomposed, becomes completely changed into sulphate of potash and carbonic acid when boiled with a solution of permanganate of potash.

Different organic sulphuretted compounds, especially hydrosulphate of sulphuret of benzoyle, behave in the same way. The authors therefore hope that this method will advantageously replace the oxidation of sulphuretted matters by the mixture of carbonate of soda and chlorate of potash, or by oxide of copper in a current of oxygen.

For certain sulphuretted compounds the employment of the permanganate presents peculiar advantages. In the analysis of the alkaline polysulphurets and hydrosulphates there is never any fear of loss of sulphur by evolution of hydrosulphuric acid, as the liquid is constantly alkaline.

In the course of their experiments the authors have observed some facts regarding the action of permanganate of potash upon various organic matters. The hydrocarbons of a low equivalent, such as benzine, reduce the permanganate in the cold with great facility, only furnishing carbonate or bicarbonate of potash. But the higher hydrocarbons furnish, together with the carbonate, some well-defined products of oxidation. Thus naphthaline furnishes phthalic acid, a product which is difficult to prepare by the methods hitherto known.

Camphor reduces the permanganate by the aid of a prolonged ebullition; camphorate of potash is formed.

Alcohol does not act very speedily upon the solid, pulverized permanganate in consequence of the slight solubility of this salt in alcohol; acetate of potash is produced. Under the same circumstances wood-spirit furnishes carbonate and formiate. Sebacic acid is converted into succinate of potash.

Stearic acid only gives a mixture of stearate and carbonate; benzoic acid has an analogous action, a portion of it forming benzoate of potash, whilst the rest is completely oxidized, forming water and carbonic acid.

Aniline reduces the solution of the permanganate in the cold; oxalate and carbonate of potash are formed.

Lastly, ammonia decomposes the solution of the reagent in the cold, nitrogen being evolved. No nitrate is formed.—*Comptes Rendus*, June 7, 1858, p. 1110.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 17, 1858. (The Lord Wrottesley, President, in the Chair.)

"Researches on the Phosphorus-Bases." By A. W. Hofmann, Ph.D., F.R.S.

In a paper published in the Transactions of the Royal Society, we (M. Cahours and myself) have given a detailed account of the preparation of the phosphorus-bases, and also an accurate description of

triethylphosphine, the most characteristic and accessible representative of this class of compounds.

The object of our joint inquiry was chiefly to examine the phosphorus-bases as a class, and to establish their analogy with the corresponding terms of the nitrogen-series. The deportment of the phosphorus-bodies in their relation to other compounds has as yet been scarcely investigated. For several months I have been engaged in this study, which promises a rich harvest of results. Most of the experiments were made with triethylphosphine, a substance which, in consequence of its convenient position in the system of organic compounds, in consequence of the variety of its attachments, the energy and precision of its action, and, lastly, the well-defined character of its compounds, will probably become an agent of predilection in the hands of the chemist.

It is my intention to trace the history of this remarkable body in its several directions; and for this purpose, in fact, a considerable amount of material has been already accumulated. But since necessarily some time must elapse before such an inquiry, which from the peculiar character of the compound is often obstructed by unusual difficulties, can be completed, I beg leave to present my results in the same measure as the inquiry advances, hoping that at a later period I may be allowed to collect the scattered observations, and to lay them in a more elaborated and digested form before the Society.

Among the numerous reactions of triethylphosphine, my attention has been chiefly directed to the compounds which this body furnishes when submitted to the action of organic chlorides, bromides, and iodides.

I. *Action of Bibromide of Ethylene upon Triethylphosphine.*

In the anhydrous condition the two bodies act even at the common temperature with considerable power upon each other, a white crystalline substance being immediately precipitated. If the reaction be allowed to go on in the presence of a large volume of anhydrous ether, the deposition of the crystalline body is considerably retarded, unless the mixture, in an appropriate apparatus, be exposed to the temperature of boiling water. After a short digestion, on distilling off the ether and the excess of bibromide, a crystalline cake is left in the retort, consisting of several bromides, the nature and the relative proportions of which appear in a great measure to depend upon the rapidity of the reaction. I have found it most convenient to work with ethereal solutions at the common temperature.

The determination of the bromine in the crystalline body revealed at once the compound character of this substance, for it steadily diminished by dissolving the bromide in absolute alcohol, and reprecipitating it partially by ether. By repeating this process four or five times, a body of constant composition was obtained.

The compound thus prepared is a crystalline mass, without odour, extremely soluble in water, and even in absolute alcohol, but insoluble in anhydrous ether. It exhibited a rather unexpected compo-

sition, for on analysis it was found to contain

$$C_{16}H_{19}PBr_2,$$

and consequently to have been formed by the simple union of 1 equiv. of triethylphosphine and 1 equiv. of bibromide of ethylene,

$$C_{12}H_{15}P + C_4H_4Br_2 = C_{16}H_{19}PBr_2.$$

The bromine in this compound exists in two perfectly different forms; addition of nitrate of silver precipitated only one-half of this element as bromide of silver, while even by protracted ebullition the second half remained untouched. The result changed, however, on digestion with freshly precipitated oxide of silver, when the whole of the bromine separated at once in the form of bromide of silver.

On adding to the solution of the bromide an excess of nitrate of silver, filtering off the bromide, and removing the excess of silver by hydrochloric acid, a corresponding chloride was obtained, from which bichloride of platinum precipitated a beautiful orange-yellow platinum-salt. In a moderately diluted solution which had been previously gently heated, no immediate precipitate was produced; but on cooling, the same salt was deposited in magnificent needles, which could be recrystallized from boiling water, or better from hydrochloric acid. This compound contained

$$C_{16}H_{19}BrPCl,\ PtCl_2.$$

A difficultly soluble gold-salt, crystallizing from boiling water in small scales, was found to have the corresponding composition,

$$C_{16}H_{19}BrPCl,\ AuCl_3.$$

Very different results were observed when the whole of the bromine was removed by means of oxide of silver. A powerfully alkaline solution was thus obtained, which, converted into hydrochlorate, gave, with bichloride of platinum, a precipitate only after very considerable evaporation. The precipitate was likewise of a deep orange-red colour; it readily dissolved in boiling water, from which it separated on cooling in the form of well-defined octahedra having the composition

$$C_{16}H_{18}PCl,\ PtCl_2.$$

Terchloride of gold furnished likewise a crystalline precipitate very similar in appearance to the gold-salt previously mentioned, but containing

$$C_{16}H_{18}PCl,\ AuCl_3.$$

The action of bibromide of ethylene on triethylphosphine, and the subsequent transformation of the compound produced, is readily explained. The two substances unite in equal equivalents, the product of the reaction being the bromide of a phosphonium, in which the fourth equivalent of hydrogen is replaced by a compound molecule, C_4H_4Br (brominetted ethyle?), of monatomic substitution-power,

Bromide of triethyl-bromethylene-phosphonium $\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\(C_4H_4Br)'\end{matrix}\right\}PBr.$

The compound phosphonium of this bromide possesses very considerable stability, as is sufficiently evinced by its deportment with nitrate of silver, and by the formation of the platinum- and of the gold-salt. All my attempts, however, to separate the base itself have entirely failed. Under the influence of oxide of silver, the bromide yields an alkaline solution possessing all the characters of the –onium-bases. The body in solution, however, no longer belongs to the same series, the elements of hydrobromic acid having separated from the original compound metal.

$$\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\(C_4H_4Br)'\end{matrix}\right\}PBr+2AgO=2AgBr+\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_3\end{matrix}\right\}PO,HO.$$

The compound thus obtained may be designated as the hydrated oxide of triethyl-vinyl-phosphonium.

I have ascertained by experiment that the brominetted bromide is by no means the only result of the action of bibromide of ethylene on triethylphosphine, although under favourable circumstances it appears to be the chief product. Invariably a portion of the bibromide, faithful to its traditions, splits into hydrobromic acid and bromide of vinyle; and we find therefore in the white crystalline mass always, together with hydrobromate of triethylphosphine, a certain quantity of the very bromide of triethyl-vinyl-phosphonium, which, as has been stated, results from the action of oxide of silver on the brominetted bromide.

$$2\left[\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}P\right]+C_4H_4Br_2=\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\H\end{matrix}\right\}PBr+\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_3\end{matrix}\right\}PBr.$$

The action of bibromide of ethylene on triethylphosphine, complex as it is, receives an additional element of complication by the influence of heat. Ebullition appears to facilitate the formation of a fourth bromide, which, although less prominently, is also produced in the cold. The study of this compound is not yet completed.

"Action of Bisulphide of Carbon on Triethylphosphine." By A. W. Hofmann, Ph.D., F.R.S.

Among the many characteristic reactions of the phosphorus-bases, their deportment with sulphur is so conspicuous that it has served frequently as a test for the presence of these substances. In continuing the study of the phosphorus-bases, I have found that this remarkable attraction for sulphur is by no means limited to this element in the free state. Many sulphur-compounds, when coming into contact with triethylphosphine, are instantaneously decomposed, their sulphur being appropriated in the formation of the beautiful bisulphide

$$E_3PS_2,$$

which, as has been pointed out on a former occasion, is generated by

the action of free sulphur. As an illustration, the deportment of bisulphide of nitrogen may be quoted. This substance, obtained by the action of ammonia on chloride of sulphur, and as yet scarcely touched upon as an agent of research, is instantaneously decomposed into its constituents when acted upon by triethylphosphine,

$$\underbrace{E_3P}_{\text{Triethyl-phosphine.}} + \underbrace{NS_2}_{\text{Bisul-phide of nitrogen.}} = \underbrace{E_3PS_2}_{\text{Bisulphide of triethyl-phosphine.}} + N.$$

The reaction is so violent that care must be taken to prevent the phosphorus-base from being inflamed.

Triethylphosphine is not less powerfully attacked by bisulphide of carbon; but the result is different. On mixing the two bodies in the anhydrous condition, they are found to combine with explosive violence, a deep crimson-coloured crystalline compound being produced. This substance is obtained in better crystals if ethereal solutions, instead of the anhydrous compounds, be employed. The new body separates in beautiful crimson leaflets the moment the two solutions are mixed. This phenomenon is so characteristic, that ever since it was first noticed, it has served me as a valuable test for the detection of even minute traces of triethylphosphine. A watch-glass, moistened with the liquid in which the phosphorus-base is suspected, is held over a vessel containing bisulphide of carbon: the vapour of this compound immediately causes the formation of a crimson network of crystals, if the smallest quantity of triethylphosphine be present. It is necessary that the base should be free; its saline solutions are not affected by bisulphide of carbon; the reaction, however, immediately appears when the base is liberated by the addition of an alkali.

The new body produced by the action of bisulphide of carbon upon triethylphosphine is insoluble in water, nearly insoluble in ether, but soluble in alcohol. From boiling alcohol it is deposited on cooling in crimson needles, somewhat similar to the crystals of chromic acid as obtained by the action of sulphuric acid upon bichromate of potassium. The presence of bisulphide of carbon in the alcohol considerably increases its solvent power for the crimson body. The new substance fuses at about 95° C.; it is volatile even at the common temperature, and is easily volatilized at the temperature of boiling water. When rapidly heated it sublimes with partial decomposition.

The crimson crystals appear to have the character of a weak base; they easily dissolve in concentrated hydrochloric acid, a colourless liquid being formed; from this solution potassa or ammonia reprecipitate the body, apparently unchanged, although, in consequence of the finely divided state, of a somewhat lighter colour. The hydrochloric solution gives with bichloride of platinum a bright yellow amorphous salt insoluble in alcohol and ether, which on drying becomes dingy, with indications of decomposition. A gold-salt similarly obtained exhibits a like deportment. Both salts

appeared but very little adapted for analysis. The alcoholic solution of the body is decomposed by nitrate of silver with formation of sulphide of silver.

The analysis of the crimson crystals has shown that they contain

$$C_{14}H_{15}PS_4 = C_{12}H_{15}P + C_2S_4 = E_3P + C_2S_4.$$

They are therefore formed by the direct union of 1 equivalent of triethylphosphine with 2 equivalents of bisulphide of carbon.

In the dry state the bisulphide of carbon compound may be preserved without being altered. In the presence of moisture, however, it is decomposed, especially during hot weather. On examining some specimens which had been kept during several months, the crimson colour was found to have disappeared, the substance had assumed a light yellow colour, and on opening the bottles the odour of sulphuretted hydrogen became at once apparent. The yellowish substance on recrystallization proved to be pure bisulphide of triethylphosphine. I leave it undecided whether this transposition had taken place according to the equation

$$E_3PC_2S_4 + 2HO = E_3PS_2 + 2HS + C_2O_2,$$

or

$$E_3PC_2S_4 + 2HO + 2O = E_3PS_2 + 2HS + C_2O_4.$$

What is the constitution of the crimson body? In mineral chemistry we are acquainted with a compound closely allied in composition and formation to the new compound. Bisulphide of carbon, when treated with an alcoholic solution of ammonia, furnishes, together with other products, a salt crystallized in long lemon-yellow needles, which is known by the name of sulphocarbamate of ammonium.

This compound,

$$(H_4N)H_2N, C_2S_4,$$

when treated with diluted acids, is converted into an oily acid of but little stability, sulphocarbamic acid:

$$HH_2N, C_2S_4.$$

If we replace in this compound the hydrogen by ethyle, the nitrogen by phosphorus, in other words, if we replace the ammonia by triethylphosphine, we arrive at the composition of the body which forms the subject of this note.

I have convinced myself experimentally that trimethylphosphine exhibits with bisulphide of carbon a perfectly similar deportment. The compound formed is likewise of a crimson colour, but of a somewhat lighter tint; it is more volatile and more readily soluble in alcohol than the corresponding ethyle-compound: it is also somewhat soluble in water.

Triethylarsine is not altered by the addition of bisulphide of carbon; after some time, however, long needles are formed in the mixture of the two bodies. These needles are probably an analogous arsenic-compound: I have not however examined them. A mixture of triethylstibine and bisulphide of carbon was preserved for several months, without undergoing any change.

THE CHEMICAL GAZETTE.

No. CCCLXXXV.—November 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Synthesis of the Hydrocarbons. *By* M. BERTHELOT.

STARTING from the study of the proximate principles which enter into the composition of living creatures, chemists have sought in the first place to convert the one into the other, by destroying them by reagents in a gradual and regular maner, passing from the primitive compound to less complicated compounds, from these to others, and thus by degrees to the simple terms of a total destruction. It is thus that from the ternary compounds, formed of carbon, hydrogen and oxygen, we pass to the carburets of hydrogen; it is thus that we group around the alcohols the greater part of the organic compounds. But we have not hitherto known how to ascend this scale, starting from the elementary bodies to form carburets of hydrogen, and then alcohols and oxygenated compounds of gradually increasing complication, simply by the action of the affinities which we are accustomed to set in operation in inorganic nature.

The examples of synthesis were so rare, so isolated, and so barren of results, that most minds were even led to regard it as chimerical to hope that in a general way organic substances could be reproduced by means of the simple bodies of which they are composed. Thus Gerhardt could say, not many years ago,—"I prove that the chemist does exactly the opposite of living nature,—that he burns, destroys, and operates by analysis; that the vital force operates by synthesis,—that it reconstructs the edifice destroyed by chemical forces."—(*Comptes Rendus*, xv. p. 498.)

Whatever might have been the speculative opinions upon this subject, no alcohol had been produced experimentally by means of a carburet of hydrogen, and no carburet had been formed out of its elements. It is this operation of synthesis that I have pursued for more than eight years, and of which the present memoir contains the starting-point.

From inorganic compounds, and by a purely chemical course, I have succeeded in forming the principal carburets of hydrogen; by the aid of general methods I have converted the carburets into alcoholic compounds. I have discovered various general processes which enable us to convert an acid or an oxygenated compound into the corresponding alcohol, a simple compound into a substance with more carbon and of a higher order of complication; in one word, all the first terms of the synthesis and the most difficult ones are already realized; the intervention of slow actions and of feeble and delicate affinities is sufficient for the attainment of the object in view. It will allow us to go still further; for in proportion as we rise to more complicated compounds, the reactions become easier and more varied, and the resources of synthesis increase at each new step.

The experiments relating to the conversion of the carburets of hydrogen into alcohols have already been developed before the Academy*; I now bring forward those appertaining to the synthesis of the following hydrocarbons:—

Marsh-gas	$C^2 H^4$;
Olefiant gas.....	$C^4 H^4$;
Propylene.....	$C^6 H^6$;
Butylene	$C^8 H^8$;
Amylene	$C^{10} H^{10}$;
Benzine	$C^{12} H^6$;
Naphthaline.....	$C^{20} H^8$.

Carbon does not combine directly with hydrogen, but we may seek to effect this combination by indirect processes, and by taking advantage of the nascent state, that is to say of the aptitude for entering into a new combination possessed by bodies at the moment when they escape from another combination.

To prevent all suspicion with regard to the origin of the primary materials employed in these experiments, the carbon was derived from purely mineral substances, and especially from carbonate of baryta, for in experiments of synthesis the results can only be regarded as conclusive when they have been obtained with perfectly definite compounds, such as gaseous, volatile or crystallized bodies, and when they have been realized by a series of operations in which reagents, agents, and solvents of a purely mineral nature have been employed. The results contained in these researches have been realized with all the rigour of the preceding conditions. But substances of organic origin, and especially carbon, have been positively excluded from these experiments, because the results to which their employment might have led would necessarily be doubtful; in fact all these substances, and especially carbon, almost constantly retain small quantities of hydrogen, and usually preserve a special structure dependent on their organic origin which cannot be reproduced at pleasure, and the influence of which upon the phænomena cannot be appreciated.

The formation of the more simple carburets of hydrogen being

* See Chem. Gaz. vol. xiii. p. 61.

demonstrated, we may form oxygenated compounds with these carburets; these compounds become in their turn starting-points for carburets of hydrogen more complicated than those from which they originated; with the new carburets corresponding oxygenated compounds are formed, and thus we rise, by a gradual and regular series of transformations, to compounds of greater and greater complication.

The totality of these results will be expounded in the following order:—

First Part.—Transformation of oxygenated compounds of carbon into carburets of hydrogen. To this will be joined some experiments tried upon nitruret of carbon and upon carburet of iron.

Second Part.—Conversion of sulphuret of carbon into carburet of hydrogen.

Third Part.—Conversion of the chlorides of carbon into carburets of hydrogen.

Fourth Part.—Formation of more complicated carburets of hydrogen by the action of heat upon the acetates and butyrates.

The following are some details of one of the experiments. Oxide of carbon was prepared by heating to redness a mixture of iron-filings and carbonate of baryta; with this gas 60 balloons of 1 litre capacity, containing potash, were filled, and kept at 212° F. for three weeks. At the end of this time the absorption of the oxide of carbon and its conversion into formiate of potash were complete. The formiate of potash was converted into formic acid, and then into formiate of baryta; the weight of the latter salt was nearly 300 grms. It was submitted to the action of heat, and furnished, amongst other products, marsh-gas, $C^2 H^4$; olefiant gas, $C^4 H^4$; and propylene, $C^6 H^6$. The two latter carburets were separated from the other gases by the action of bromine, then regenerated from their bromides by processes of inverse substitution, and submitted to direct analysis.

For greater certainty, the olefiant gas thus regenerated was converted into sulphovinic acid and sulphovinate of baryta.

In another experiment made with 2 kilogrms. of ordinary formiate of baryta, benzoic æther and alcohol were also formed.

Thus in the preceding series of experiments, the execution of which lasted for several months, the carbon contained in the carbonate of baryta, after having been changed successively into oxide of carbon, formiate of baryta, olefiant gas, the bromide of this gas, and into olefiant gas for the second time, and lastly into sulphovinic acid and sulphovinate of baryta,—after having passed through two successive combinations, and been five times in the gaseous state, without even being in contact with any organic substance, is definitively fixed in a crystallized organic compound, the conversion of which into alcohol presents no difficulty. This experiment, therefore, completely demonstrates the formation of alcohol by means of purely mineral elements; carbonate of baryta and water are the only compounds which have furnished their elements to the alcohol formed.

To show exactly in what proportions this formation of carburets of hydrogen takes place, it will suffice to say that 60 litres of oxide of carbon furnished about 3 litres of marsh-gas, and ½ litre of olefiant gas; these are the numbers obtained in the experiments which resulted in the formation of these hydrocarbons by means of mineral elements.—*Comptes Rendus*, June 7, 1858, p. 1102.

Note on the Sulphuric Derivatives of the Vegetable Alkaloids.
By P. SCHUTZENBERGER.

Quinine and cinchonine dissolve in fuming sulphuric acid. If the liquor is diluted after an interval with water, ammonia no longer produces a precipitate. The other vegetable alkaloids behave in the same way. I have studied the reaction particularly in the case of the above two bases.

The sulphuric solution, very much diluted with water, was saturated with baryta; the liquor separated from sulphate of baryta by filtration, and evaporated in the water-bath, furnished in both cases a colourless syrup, which soon dried into a vitreous, transparent, and friable mass, soluble in water in all proportions, but by no means deliquescent, of a slightly bitter taste, more marked than in the case of quinine. These two substances are the baryta-salts of the two acid sulphuric derivatives of quinine and cinchonine; they may be called sulphoquinic and sulphocinchonic acids.

Indeed, when these two products are burnt with pure nitre, and the residue washed with water, sulphate of baryta remains, and the washing-water contains no sulphuric acid.

The sulphuric acid and the baryta occur in equivalent proportions.

Sulphoquinate of baryta, dried at 212°, and experiencing no further loss at a higher temperature, gave after incineration sulphate of baryta corresponding to 27·02 per cent., which leads to the formula

$$C^{40}\,H^{23}\,N^{2}\,SO^{3}\,BaO.$$

Theory requires 26·99 sulphate of baryta.

Sulphocinchonate of baryta, dried at 212°, gave sulphate of baryta 28·13 per cent., leading to the formula

$$C^{40}\,H^{23}\,N^{2}\,O,\,SO^{3}\,BaO.$$

Theory requires 28·03 sulphate of baryta.

The two corresponding acids are obtained by precipitating the baryta with an equivalent quantity of sulphuric acid. They are solid, uncrystallizable, of an acid taste, soluble in all proportions in water, soluble in alcohol. They are represented by the formulæ

$$C^{40}\,H^{23}\,N^{2}\,O^{3}\,SO^{3},\,HO,$$
$$C^{40}\,H^{23}\,N^{2}\,O\;\;SO^{3},\,HO,$$

which only differ from those of the basic sulphates of quinine and cinchonine by one equivalent less of water.

The constitution of these compounds is another argument in favour of the formula

$$C^{13}\,H^{21}\,N^{2}\,O^{4}\text{ or }O^{2},$$

adopted by most chemists.

The same reaction applying to other alkaloids, each of them would have a corresponding sulphoconjugate acid of the form $(\overset{+}{A}SO^3)$.—*Comptes Rendus*, August 2, 1858, p. 235.

On some Compounds of Chloral, and the Formation of Chloralide
By G. STÄDELER.

At the author's instigation Kyburg has made some experiments upon the production of compounds of chloral. He succeeded in preparing

Chloralammonia, a compound which, like aldehyde-ammonia, reduces silver in the form of a speculum. From this body sulphuretted hydrogen throws down a substance containing sulphur, which is probably to be arranged beside thialdine. If sulphuretted hydrogen be allowed to act upon an aqueous solution of chloral, a crystalline compound which dissolves with difficulty separates; this may be compared with acetyle-mercaptan, but is far more readily decomposable, as it loses sulphuretted hydrogen even during drying. By boiling hydrate of chloral with hydrocyanic acid and muriatic acid, a syrupous acid, resembling lactic acid, is obtained; and it is also easy to produce crystalline compounds of chloral with bisulphite of soda and ammonia.

Since the period when the author gave the formula $C^{10}H^2Cl^6O^6$ to chloralide, that substance has received three others, namely—

$C^{12}H^3Cl^7O^8$ from Gerhardt, $C^8HCl^5O^4$ from Laurent, and $C^8H^2Cl^5O^5$ from Gmelin. Kyburg has determined the chlorine in freshly prepared products. Gerhardt's formula requires 64·13 per cent., Laurent's 68·67 per cent., and the author's 65·94 per cent. Kyburg's analysis agreed with the author's former statements.

The author has also found that chloralide is produced from chloral by concentrated sulphuric acid (consequently without the cooperation of water). He therefore now explains its formation in the following way:—

$$3\,C^4HCl^3O^2 = HCl + C^2Cl^2 + C^{10}H^2Cl^6O^6.$$
Chloral. Chloroform. Chloralide.

Consequently there would be produced in the first place the triatomic modification of chloral, insoluble chloral, and this would become decomposed into chloralide and chloroform, or instead of these into protochloride of carbon and muriatic acid. By operating on a large scale it is in fact observed that perfectly fluid chloral, once treated with sulphuric acid, solidifies almost instantaneously on the addition of a fresh amount of sulphuric acid, in the form of insoluble chloral, and the decomposition of the latter into chloroform and chloralide reminds us of the decomposition which it undergoes by fixed alkalies; in this case also chloroform is produced, but the decomposition goes much further.—Liebig's *Annalen*, cvi. p. 253.

Note on the Action of Aqueous Vapour and Oxide of Carbon upon some Sulphates. By E. JACQUEMIN.

When a current of aqueous vapour and oxide of carbon is passed over sulphate of potash, soda, magnesia, strontia, or baryta at a red heat, there is an evolution of carbonic acid and sulphuretted hydrogen, and the oxides are produced. The aqueous vapour carries away sulphur in a state of extreme division, for sulphuretted hydrogen may be partially destroyed at the temperature of the experiment.

The final result is brought about by two successive reactions. The reducing agent first converts the sulphate into sulphuret, in accordance with the general equation

$$MO, SO^3 + 4CO = MS + 4CO^2.$$

The author has obtained sulphuret of sodium by passing dry oxide of carbon over sulphate of soda at a high temperature, and has even formed sulphuret of magnesium of great whiteness by operating in the same way upon sulphate of magnesia.

The aqueous vapour afterwards intervening furnishes sulphuretted hydrogen and hydrate of the base, for

$$MS + 2HO = MO, HO + HS.$$

In case these facts should receive an industrial application, the production of oxide of carbon would cause no embarrassment, for it would be sufficient to pass over the sulphates the gases arising from furnaces. If baryta, for example, should find extended applications, it would be easy to found a process for its manufacture upon the above facts. The calcination of the nitrate, the method at present adopted, is expensive, although the nitrous products of this decomposition are made use of. The process proposed by the author is far less troublesome; the sulphur and sulphuretted hydrogen formed would furnish sulphurous acid by combustion, and this would serve for the production either of sulphite of soda or of sulphuric acid.

This application of the sulphur is of great importance. In the manufacture of soda by Leblanc's process all the sulphur passes into the state of oxysulphuret of calcium, a product of no value, which encumbers the manufactories and, under the influence of the carbonic acid and humidity of the atmosphere, gives rise to noxious emanations. In the author's process all the sulphur would be employed in the manufacture of sulphuric acid, which would be again used in the factory for producing sulphate of soda and afterwards artificial soda.—*Comptes Rendus*, June 14, 1858, p. 1164.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Industrial Applications of Baryta. By F. KUHLMANN.

THE author has already called attention to the utility of sulphate of bartya in painting in distemper and silicious painting, especially as

the substitution of this white compound for white lead and zinc white is not only supported by considerations of economy, inalterability, and durability, but also by considerations of hygiene. This double advantage has led the author to persevere in the endeavour to produce sulphate of baryta at a cheap rate on a large scale, and the present paper contains the first portion of his results.

To obtain artificial sulphate of baryta at a moderate price, the first point was to reduce the price of the acids which constitute the principal expense of its manufacture. With this view, the author has endeavoured to condense the acid vapours more completely, as a portion of them is lost in the soda manufactories to the great prejudice of the manufacturers, the public health, and vegetation.

By placing native carbonate of baryta (Witherite) in contact with the vapours escaping from the furnaces for the decomposition of common salt, or from our leaden chambers, after their condensation has been effected under ordinary conditions, the author has succeeded in retaining a great portion of the uncondensed vapours. The baryta dissolved by these acids is converted into sulphate by an addition of sulphuric acid, and the muriatic or nitric acids thus condensed and isolated, are returned into the condensing apparatus of which they increase the profits.

There is a much greater loss of muriatic acid than that caused by the imperfection of condensing apparatus, namely that which necessarily takes place in the manufacture of chlorine or of chloride of lime, which constitutes the principal use of muriatic acid. In this manufacture more than half the muriatic acid employed is lost in the form of chloride of manganese. In practice, from the impurity of the oxide of manganese, this loss rises to two-thirds, and becomes of great importance. The author calculates the amount of loss in France alone at two millions of francs (£800,000). Many attempts have been made to turn the residues of the manufacture of chlorine to some account; the chloride of manganese has been applied to the purification of gas, to the production of ammoniacal salts, to the purpose of disinfection in some systems of sewerage; and lastly, some attempts have lately been made, in the great manufactory of Mr. Tennant near Glasgow, to regenerate the oxide of manganese, and render it capable of again producing chlorine, but all these applications are insignificant compared with the great quantity of residue produced.

The liquid residues of the manufacture of chlorine have also generally formed serious embarrassments in chemical factories, and have even been productive of danger to the public health, whether they were allowed to flow into streams of water, or caused to penetrate into the soil by means of absorbing wells.

After the condensation of the acids lost in the atmosphere, the author turned his attention to the utilization of those contained in the liquid residues; and he has succeeded in effecting this completely, by availing himself of a reaction analogous to that which permitted Leblanc to endow France with the manufacture of artificial soda. In Leblanc's process a mixture of suitable proportions

of sulphate of soda, chalk, and charcoal, is converted under the influence of a high temperature into insoluble oxysulphuret of calcium and carbonate of soda, which is easily isolated in consequence of its solubility.

In the author's process a mixture of suitable proportions of native sulphate of baryta, chloride of manganese and charcoal, is converted in the same way into insoluble sulphuret of manganese and chloride of barium, which is easily separated by lixiviation. The reaction may be expressed by the following formula:—

$$BaO, SO^3 + MnCl + 4C = BaCl + MnS + 4CO.$$

An analogous reaction may likewise be established for the chloride of iron which always accompanies the chloride of manganese. The charcoal always acts as a deoxidizing agent, and becomes converted into oxide of carbon.

After some trials to ascertain a good proportion, the author arrived at a result which exceeded his hopes, allowing the native sulphate to be converted into chloride of barium, without a greater loss than 3 or 4 per cent. of the sulphate employed.

The mode of operation is as follows:—The transformation above mentioned is effected in large reverberatory furnaces, of the same construction as the soda-furnaces, or, what is better, the furnaces for the decomposition of common salt, in which the bed is divided into two compartments by a low ridge. When these furnaces have been heated for some time, a finely powdered mixture of native sulphate of baryta and coke is introduced into the compartment furthest from the fire; over this is poured the crude residue of the manufacture of chlorine, after its excess of acid has been saturated with a little chalk or native carbonate of baryta. The action of the heat upon this mass thickens it by degrees. When brought to the condition of a firm paste, it is pushed by means of suitable iron instruments, over the separating ridge, into the compartment nearest to the fire. Here the mass swells up, and soon emits small flames of oxide of carbon, like those which are observed at a certain period in the soda furnaces, but which derive a slight greenish colour from the baryta. After an hour of calcination at a red heat, a semifluid paste, of rather more consistency than crude soda, is turned out; on cooling, this furnishes a black mass, formed of chloride of barium, a little hyposulphite of baryta, and sulphurets of manganese and iron. After exposure to the air for a few days this crude chloride of barium becomes disaggregated; the hyposulphite contained in it passes to the state of sulphate. The lixiviation is then effected by the aid of heat in the apparatus usually employed in the lixiviation of soda.

The product of this lixiviation consists of a perfectly clear solution of nearly pure chloride of barium. If there be a slight excess of sulphuret of barium, giving it a yellowish colour, this is removed by the addition, until complete decolorization, of a solution of chloride of manganese, the residue of the manufacture of chlorine, from which all the chloride of iron has been separated by a previous

digestion with native carbonate of baryta. If, on the contrary, there is a slight excess of the salt of manganese, it is got rid of by a little sulphuret of barium.

A circumstance of some interest, especially in a scientific point of view, is that in clearing out a furnace, the author found that in the part of this furnace where the sulphate of baryta was nearest to the grate, and where at the same time it was in contact with the brick, there was an abundant deposit of a green and blue matter, containing no soda, manganese or cobalt, and which appeared to be an ultramarine in which baryta replaced the soda. The author calls attention to the fact, that before the *Société d'Encouragement* proposed a prize for the discovery of a means of manufacturing artificial ultramarine, M. Tassart had indicated the production, in a soda furnace, of a blue matter which M. Vauquelin recognized as ultramarine, and that soon after this first observation he noticed the production of the same artificial ultramarine, under circumstances which rendered the explanation of the phænomena of its formation less difficult, in a portion of the furnaces for the calcination of sulphate of soda, where this sulphate was in contact with the bricks at a high temperature.

The first observation of the existence of a barytic ultramarine, under analogous circumstances, would furnish another proof that the germ of a discovery may lie in an attentive examination of some fragments of a furnace in course of demolition.

Manufacture of artificial sulphate of baryta.

This is the first and most important application which the author has made of his method of utilizing the residues of the manufacture of chlorine.

The solution of chloride of barium, obtained by the lixiviation of the crude chloride, has a density of 24°—25° B. When it has been purified as above described, it is put into large tubs and mixed with sulphuric acid from the lead chambers, diluted with water until it only marks 30° of Beaumé's areometer. The acid is added until no more white precipitate is formed in the liquid. The whole is then well stirred and left to settle. The sulphate of baryta soon separates, when the supernatant fluid may be drawn off by a siphon; it consists of muriatic acid marking 6° B.

The artificial sulphate thus obtained is washed to remove the last traces of free acid; it is then converted into a firm paste by filtration through a bag. The expulsion of the water is facilitated by pressure or by centrifrugal action. When the paste is sufficiently firm, it is put into casks for sale; in this state it contains 30—32 per cent. of water.

Its desiccation and manufacture into cakes may be effected by the processes employed with white lead; but it is to be remarked that, for most purposes, it is advantageously kept in the form of paste, as after much desiccation it does not easily acquire the state of division which it possessed at the moment of its precipitation.

With regard to the applications of sulphate of baryta, the author remarks that it is a very unexpected property of this salt that it appears to enter into a slow but intimate combination with the soluble alkaline silicates, and that independently of its capability of being applied by means of these salts to produce painting of incomparable whiteness, presenting a certain lustre, and entirely unalterable by sulphuretted hydrogen; it may also serve to facilitate the fixation of other colours. Thus painting done with a mixture of zinc-white and sulphate of baryta, possesses such solidity and adhesive power that it may be safely applied over old oil paint. The experiment has been made in Lille on a very large scale. This is a result of great importance for most large towns in which houses of any consequence are covered with oil paint, which is costly and requires to be frequently renewed.—*Comptes Rendus*, September 6, 1858, p. 403.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Leeds, September 23rd, 1858.

On the Carbonates of Alumina, Chromic Oxide, and Ferric Oxide. *By* Dr. WALLACE, F.C.S., *Glasgow.*

THE endeavour to ascertain the true nature of the combinations which carbonic acid forms with the three best known sesquioxides, has furnished subject of research to several eminent chemists; but, unfortunately, the results which have been obtained have differed so widely, that each new investigator has only served to throw the whole matter into greater confusion and uncertainty. In addition to these discrepancies, which are owing, probably, to the different modes of preparation adopted, the existence of carbonates of alumina and ferric oxide has been altogether denied by several authorities.

The investigation, the results of which are embodied in the present paper, was undertaken with the object of ascertaining the maximum amount of carbonic acid with which the several sesquioxides can be made to combine. The precipitates were prepared with cold and highly diluted solutions, washed with cold water, and dried at the ordinary temperature of the air, over oil of vitriol. The preparation was exceedingly tedious, the washing occupied several weeks, and the desiccation about as long a time.

The process generally adopted was to precipitate the chlorides of the respective metals by a solution of carbonate of soda; a specimen of chromic carbonate was also prepared with carbonate of ammonia. The process of analysis consisted of a modification of the improved method of conducting organic analysis. The oxides resulting from the application of heat were analysed with great care; and all the

compounds in the preparation of which carbonate of soda had been employed, showed not inconsiderable traces of the precipitant. Weeks of washing did not suffice to remove the contamination, nor did levigation of the dried powders, and continued digestion with distilled water, add much to the purity of the preparations. I have been induced to believe that the soda exists as bicarbonate, and I have therefore calculated it as such, and deducted the proportions of carbonic acid and water from the quantities obtained by experiment. These corrections, although small in amount, are essential to the accuracy of the results

From the analysis of several preparations of the same carbonate containing various quantities of the precipitating agent, I have arrived at the conclusion that protracted washing, while it removes a portion of the precipitant, also decomposes the carbonate of the sesquioxide in some degree, although not by any means in proportion to the quantity of precipitant removed. The chromic compound formed with carbonate of ammonia gave results almost identical with those obtained with the salt prepared with carbonate of soda.

I have observed a property of these carbonates which is worthy of attention: they absorb, with peculiar avidity, minute quantities of lime existing in the washing-water. This property also pertains, although to a smaller extent, to the hydrated sesquioxides. I have found that ferric oxide, even if precipitated by pure ammonia at a boiling heat, invariably carries with it a portion of lime, if that base exists in the solution, and to such an extent as to affect, in a sensible degree, the accuracy of analyses of ordinary clayband ironstones, and other minerals containing iron and lime.

Carbonate of Alumina.

This was prepared from chloride of aluminium and carbonate of soda. After having been washed and dried, it was levigated and washed again. It was kept over oil of vitriol until no further loss of weight was experienced. Analysis gave,—

Alumina.....	56·19	3=153	55·04
Carbonic acid....	14·26	2= 44	15·83
Water.....	29·55	9= 81	29·13

$3Al^2O^3, 2CO^2+9HO$, or $2(Al^2O^3, CO^2+3HO)+Al^2O^3, 3HO$.

The precipitate suffered only a minute loss of weight on being heated in the water-bath. Muspratt found $3Al^2O^3, 2CO^2+16HO$; Langlois obtained $8Al^2O^3, 3CO^2+40HO$; Th. Saussure found no carbonic acid whatever. The deficiency in the carbonic acid in my analysis may be ascribed to partial decomposition, arising from very protracted washing.

Carbonate of Chromic Oxide.

Grayish-green powder. The first two analyses are of the preparation obtained with carbonate of soda, and dried over oil of

vitriol; the third is of that precipitated by carbonate of ammonia, and dried first in the air, and then at 212°.

	I.	II.	III.		
Chromic oxide	58·07	56·87	57·33	1=77	57·03
Carbonic acid	15·86	15·31	15·56	1=22	16·30
Water	26·07	27·82	27·11	4=36	26·67

Cr^2O^3, CO^2+4HO.—Loses a mere trace of water at 212°. Meisner affirms that the carbonic acid is evolved at 62° (C.), which is evidently an error. Lefort states that it loses three-fourths of its water between 75° and 150° (C.), while the carbonic acid and the last equivalent of water are not yielded up until the temperature exceeds 300°. My experiments agree with these results. Berzelius gives as the composition of chromic carbonate $4Cr^2O^3, CO^2+3HO$; Langlois $2Cr^2O^3, CO^2+6HO$; Meisner $10Cr^2O^3, 7CO^2+8HO$; Lefort Cr^2O^3, CO^2+4HO.

Carbonate of Ferric Oxide.

The following results were obtained with the precipitate prepared with carbonate of soda, and dried at the temperature of the air:—

Ferric oxide	75·28	3=240	75·95
Carbonic acid ..	6·97	1= 22	6·96
Water	17·75	6= 54	17·09

$3Fe^2O^3, CO^2+6HO$, or $Fe^2O^3, CO^2+2(Fe^2O^3, 3HO)$.—An analysis of a specimen dried at 212° gave,—

Ferric oxide	80·07	3=240	80·54
Carbonic acid ..	6·76	1= 22	7·37
Water	13·17	4= 36	12·09

$3Fe^2O^3, CO^2+4HO$, or $Fe^2O^3, CO^2+2(Fe^2O^3, 2HO)$.—A specimen was prepared with ferric nitrate, and washed until only a very minute trace of soda existed in it. This preparation was many weeks in contact with water, and was twice dried, levigated, and rewashed. Analysis gave,—

Ferric oxide	85·10	9=720	81·7
Carbonic acid ..	2·71	1= 22	2·6
Water	12·19	12=108	12·7

$9Fe^2O^3, CO^2+12HO$, or $Fe^2O^3, CO^2+4(2Fe^2O^3, 3HO)$.—Soubeiran found a specimen exposed in a damp cellar for half a year to contain $5Fe^2O^3, 2CO^2+12HO$; Gmelin found no carbonic acid whatever; Langlois obtained, in 100 parts, 88·47 oxide of iron, 1·36 carbonic acid, and 10·17 water (dried at 212°).

The experiments of Wittstein have shown that ferric hydrate contains, when recently precipitated and dried without heat, three equivalents of water; and that by continued contact with water one half is separated, and the hydrate contains $2Fe^2O^3, 3HO$. The

composition of ferric hydrate, dried at 212°, is stated by Breithaupt and Gmelin to be $Fe^2O^3, 2HO$. The change in the state of hydration appears to exert an influence on the affinity of the oxide for carbonic acid.

In conclusion, I may state that my results confirm Muspratt's analysis of carbonate of alumina, Lefort's of chromic carbonate, and Sonbeiran's of ferric carbonate.

The extreme difficulty of removing by washing the carbonates of the alkalies, and the avidity with which lime is absorbed from its solutions, point to the probable existence of double salts similar to the compounds which the hydrates of the sesquioxides form with the hydrates of the alkaline earths. Want of time has obliged me to postpone the further investigation of this interesting inquiry.—*Communicated by the Author.*

On the Annual yield of Nitrogen per Acre in different Crops. *By* J. B. Lawes, F.R.S., F.C.S., *and* J. H. Gilbert, Ph.D., F.C.S.

In a paper given last year at the Dublin Meeting, on the question of the Assimilation of Free Nitrogen by Plants, and some allied points, the authors had stated in general terms, that the amount of nitrogen yielded per acre, per annum, in different crops—even when unmanured—was considerably beyond that annually coming down, in the forms of ammonia and nitric acid, in the yet measured and analysed aqueous deposits from the atmosphere. The investigations then referred to were still in progress; and a desirable introduction to the record of the results would obviously be, to illustrate by reference to direct experiment, that which had been before only assumed, regarding the yield of nitrogen in our different crops. To this end, had been determined, the annual produce of nitrogen per acre, in the case of various crops, which were respectively grown for many years consecutively on the same land; namely, wheat, 14 years; barley, 6 years; meadow hay, 3 years; clover, 3 years out of 4; beans, 11 years, and turnips, 8 years. In the majority of the instances referred to, the yield of nitrogen had been estimated, both for the crop grown without manure of any kind, and for that with purely mineral manure—that is, excluding any artificial supply of nitrogen. It was the object of the present communication to give a summary view of some of the facts thus brought to light.

Beans and clover were shown to yield several times as much nitrogen per acre as wheat or barley. Yet the growth of the leguminous crops, *carrying off* so much nitrogen as they did, was still one of the best preparations for the growth of wheat; whilst *fallow* (an important effect of which was the accumulation within the soil of the available nitrogen of two years into one), and *adding nitrogenous manures*, had each much the same effect in increasing the produce of the cereal crops.

Other experimental results were adduced, which illustrated the fact, that 4 years of wheat, alternated with *fallow*, had given as much nitrogen in the 8 years as 8 crops of wheat grown consecu-

tively. Again, 4 crops of wheat, grown in alternation with *beans*, had given nearly the same amount of nitrogen per acre as the 4 crops grown in alternation with fallow; consequently, also much about the same as the 8 crops of wheat grown consecutively. In the case of the alternation with *beans*, therefore, the whole of the nitrogen obtained in the beans themselves was over and above that which was obtained during the same series of years in wheat alone, whether it was grown consecutively, or in alternation with fallow.

Interesting questions arose, therefore, as to the varying sources, or powers of accumulation, of nitrogen in the case of crops so characteristically differing from one another as those above referred to.

It had been found that the leguminous crops, which yielded in their produce such a comparatively large amount of nitrogen over a given area of land, were not specially benefited by the direct application of the more purely nitrogenous manures. The cereal crops, on the other hand, whose acreage yield of nitrogen under equal circumstances was comparatively so small, were very much increased by the use of direct nitrogenous manures. But it was found that, over a series of years, only about $\frac{4}{10}$ths of the nitrogen annually supplied in manure for wheat or barley (in the form of ammonia-salts or nitrates), were recovered in the immediate increase of crop. Was any considerable proportion of the unrecovered amount drained away and lost? Was the supplied nitrogenous compound transformed in the soil, and nitrogen in some form evaporated? Did a portion remain in some fixed and unavailable state of combination in the soil? Was ammonia, or free nitrogen, given off during the growth of the plant? Or, how far was there an unfavourable distribution, and state of combination, within the soil, of the nitrogenous matters applied directly for the cereal crops—those such as the leguminous crops, which assimilated so much more, gathering with greater facility, and from different ranges of soil, and leaving a sufficient available nitrogenous residue within the range of collection of a succeeding cereal crop? These questions, among others which their solution more or less involved, required further elucidation, before some of the most prominent of agricultural facts could be satisfactorily explained.

Comparing the amount of nitrogen yielded in the different crops, when grown without nitrogenous manures as above referred to, with the amount falling in the measured aqueous deposits, as ammonia and nitric acid, it appeared, taking the average result of the analysis of three years' rain, that all the crops yielded considerably more, and some very much more, than so came down to the soil. The same was the case when several of the crops had been grown in an ordinary rotation with one another, but without manure, through two or three successive courses. Was this observed excess in the yield over the yet measured sources, at all materially due merely to exhaustion of previously accumulated nitrogenous compounds within the soil? Was it probably attributable chiefly to the absorption of ammonia or nitric acid, from the air, by the plant itself, or by the soil? Was there any notable *formation* of ammonia or nitric

acid, from the free nitrogen of the atmosphere? Or, did plants generally, or some in particular, assimilate this free nitrogen?

As already intimated, some of the points which had been alluded to were at the present time under investigation; the authors having in this, the able assistance of Dr. Pugh. Others, it might be hoped, would receive elucidation in the course of time. There of course still remained the wider questions—of the original source, and of the distribution and circulation, of *combined nitrogen*, in the soil, in animal and vegetable life on the earth's surface, and in the atmosphere above it?—*Abstract communicated by the Authors.*

Royal Society.

June 17, 1858. (The Lord Wrottesley, President, in the Chair.)

"Further Remarks on the Organo-metallic Radicals, and Observations more particularly directed to the isolation of Mercuric, Plumbic, and Stannic Ethyle." By George Bowdler Buckton, Esq., F.R.S.

Before again entering on the subject of the organo-metals, the author wishes to call attention to the remarks he has previously made* on the difficulties which presented themselves at that time in the preparation of mercuric ethyle. Secondary decompositions, induced by the nature of the materials employed and the high temperature necessary to the reaction, showed themselves even in the more easily prepared mercuric methyle, and reduced the quantity obtained considerably below that pointed out by theory.

The loss sustained in the similar operation of distilling together cyanide of potassium and iodide of mercurous ethyle, $C_4 H_5 Hg_2 I$, is yet more marked; and it may be remembered that the portion obtained did no more than suffice for a cursory examination of its most marked characters. A new mode of operating was therefore desirable, and it was not long before the following considerations presented themselves.

The powerful and well-defined affinities of zinc-ethyle have already furnished a valuable key to the explanation of several chemical problems, and seem to be well suited for experiment in the present case. Bearing in mind its well-known reactions on water and hydrochloric acid, there appeared to be well-grounded reasons for supposing that interesting decompositions might be effected with various oxides, chlorides, and iodides.

Through the instrumentality of zinc-ethyle the author has succeeded in isolating, in a neat and efficient manner, several of the organo-metals, and he indulges a hope that they may, when taken as starting-points of investigation, prove of service in fixing exact formulæ to some of those bodies, the composition of which, at present, appear doubtful from their complexity.

* Phil. Trans. Roy. Soc.; Proc. Roy. Soc. vol. ix. p. 91.

Action of Zinc-ethyle on Mercuric Chloride.

Corrosive sublimate acts with great energy on zinc-ethyle; so much so, as to render it necessary to cool the apparatus in water, and add the well-dried salt by degrees. An excess of the latter must be avoided, since chloride of mercurous ethyle would be formed, as was formerly shown to be the case in the methyle series.

After the two bodies have been brought together in their proper proportions, heat is applied, and the radical passes over by distillation as a heavy, colourless, and nearly inodorous liquid; the slight excess of zinc-ethyle is then decomposed by the addition of water, and just sufficient dilute hydrochloric acid added as will dissolve the precipitated oxide of zinc.

The two transformations may be seen in the equations,

$$C_4 H_5 Zn + Hg Cl = C_4 H_5 Hg + Zn Cl,$$

and again,

$$C_4 H_5 Hg + Hg Cl = C_4 H_5 Hg_2 Cl.$$

The pure radical boils at a temperature between 158° and 160° C. It burns readily, with a luminous and somewhat smoky flame, with disengagement of mercurial vapour. It is almost wholly insoluble in water. Alcohol dissolves it rather sparingly, but it mixes freely with ether.

The behaviour of acids towards mercuric ethyle is strictly analogous to that shown by mercuric methyle. With dilute acid there is but little change, but warm concentrated hydrochloric or sulphuric acid liberates hydride of ethyle in sufficient quantity to permit of its inflammation through a gas jet. The salts of mercurous ethyle remain in solution.

The specific gravity of a specimen boiling between 158° and 160° C. was found to be 2·444, and the same sample when submitted to analysis, gave numbers agreeing accurately with the formula

$$C_4 H_5 Hg.$$

The correctness of this formula was further confirmed by an appeal to the vapour-density.

The first experiment failed, from the circumstance that the vapour decomposes with a slight explosion, when heated a few degrees above 205° C. In this experiment metallic mercury was deposited on the walls of the glass balloon as a grey film, and the other contents consisted of an inflammable gas. Mercuric ethyle appears therefore to be resolved at this temperature into ethyle gas and mercury.

Another experiment was more successful, and gave the number 9·97 for the vapour-density.

The equivalent weight of mercuric ethyle is 129, which, being divided by the former figures, gives $\frac{129}{9·97} = 12·94$. If the constituents of this radical be condensed into two volumes of vapour, the more accurate number 14·86 should have been obtained.

The theoretical density of mercuric ethyle, thus calculated, is equal to $\frac{129}{14{\cdot}86}=8{\cdot}68$*.

This portion of the subject would be incomplete unless a few words were added on the behaviour of zinc-ethyle towards mercurous chloride.

It has been mentioned, that all attempts to reduce iodide of mercurous methyle to the form of a radical containing one equivalent of methyle and two equivalents of mercury have hitherto failed.

Reasoning *a priori*, we should not expect to find a departure in the present case, neither does such appear. Mercurous chloride reacts with vigour on zinc-ethyle, but metallic mercury is formed simultaneously with chloride of zinc and mercuric ethyle.

The decompositions of mercurous and mercuric chlorides or iodides, are thus shown:—

$$C_4 H_5 Zn + Hg_2 Cl = C_4 H_5 Hg + Zn Cl + Hg,$$

and

$$C_4 H_5 Zn + Hg Cl = C_4 H_5 Hg + Zn Cl.$$

Having succeeded, by these simple means, in effecting a replacement in zinc-ethyle through the ordinary metallic chlorides, there remained yet one point untouched, viz. the behaviour of various organo-metallic salts, under similar treatment.

First in order was tried

The Action of Zinc-ethyle on Iodide of Mercurous Ethyle.

Carbonic acid, or ordinary coal-gas, was slowly passed through the neck of a retort; and when the atmospheric air was displaced, about two ounces of zinc-ethyle, nearly free from ether, and wholly so from iodide of ethyle, was introduced. Iodide of mercurous ethyle was then added, by degrees, through the tubulure, and the whole mixed by agitation. The zinc-ethyle at first dissolves the iodide, but subsequently a cake of iodide of zinc is formed. Distillation was then commenced, the heat being raised by degrees until gaseous products appeared. The distillate, after being well washed, was rectified by the thermometer, and in this manner the radical was obtained in a state of purity. Iodide of mercurous ethyle may be formed so easily by diffused daylight, and its action is so gentle on zinc-ethyle, that its use offers greater conveniences to the operator than are afforded by any of the substances previously mentioned.

For obvious reasons, a similar choice of materials is recommended for preparing mercuric methyle.

* Here it is fitting to mention an error that has crept into the calculation of the vapour-density of mercuric methyle as it appears printed in the 'Proceedings of the Royal Society.' A false figure in the denominator of one of the fractions, causes the experimental density to appear as 14·86, whereas the true experimental density observed was 8·29. The theoretical density of mercuric methyle calculated for two volumes, equals $\frac{115}{14{\cdot}46}=7{\cdot}95$.

Action of Zinc-ethyle on Chloride of Lead.

The close relations which exist between the three metals, lead, mercury, and silver, in their equivalent weights, salts, and other characters, lead the author to anticipate success in forming their ethyle bases.

The existence of the lead radical might indeed be considered as certain, since various salts of complicated structure have been made known to chemists through the experiments of M. Löwig, on the alloy of lead and sodium, under treatment with iodide of ethyle.

The principal product obtained by him, and the only one apparently analysed, had a grouping similar to a sesquichloride. The formula ascribed by him to the radical plumbethylium is $Pb_2 (C_4 H_5)_3$. I have attempted to form the iodide of this radical by exposing sealed tubes, containing granulated lead and iodide of ethyle, to the sun's rays, but without success. No better result was obtained by substituting bromide of ethyle for the iodide, and no change could be induced even when these tubes were heated strongly with high-pressure steam.

M. Löwig's method was not resorted to, from the supposition that the action of zinc-ethyle on a mixture would only give rise to radicals of various constitution, which it might be impossible afterwards to separate, except by working on a large scale, which, considering the costliness of the materials, had its disadvantages. Perhaps success might attend the use of one of Dr. Frankland's mirrors for concentrating the sun's rays.

For obtaining the lead-radical, recourse was had to well-dried chloride of lead, which was introduced into a flask containing zinc-ethyle. The chloride immediately turned black, from the deposit of metallic lead, whilst moderate heat was disengaged. An excess of chloride was used, and the mass incorporated by stirring with a glass rod. After applying a gentle heat for a few minutes, the floating clear liquid was pipetted off. This substance is apparently a compound of zinc-ethyle and the lead radicals. It fumes slightly in the air, and no digestion with chloride of lead appeared to resolve it entirely into the lead base.

A great part of the zinc-ethyle, however, is removed by subsequent distillation; but the temperature should not be permitted to rise above 140° or 150° C. The substance in the retort is then treated with water and dilute hydrochloric acid, when the radical separates, and sinks in the form of colourless drops. When distilled cautiously, the thermometer soon rises to 200°; but beyond this point the vapour is very prone to decomposition, with deposit of metallic lead.

From this tendency to change, there is some difficulty in obtaining the substance wholly pure from bodies with lower boiling-points. The larger portion came over between 198° to 202°. Its specific gravity was found to be 1·55.

Analysis led to the formula

$$Pb\,C_8\,H_{10}, \text{ or } Pb\,(C_4\,H_5)_2.$$

It should, however, be noticed that a trifling excess in the per-

centage of carbon obtained, showed an increase rather than a decrease in the number of equivalents of ethyle.

This radical, for which the provisional name of plumbic bis-ethyle is suggested, is a colourless fluid, possessing little or no odour. It is insoluble in water, but perfectly miscible with ether. It burns readily with a beautiful orange-coloured flame, edged with blue, and gives off fumes of oxide of lead.

The radical appears to be incapable of forming salts without a partial decomposition. With weak acids there is no perceptible action; but when they are concentrated and gently heated, a gas is given off, and crystalline salts are produced.

The chloride is insoluble in water, but soluble in alcohol and in ether, from which last liquid it crystallizes in satiny needles, which are very volatile and provoke sneezing and lachrymation. It burns with the characteristic lead flame, and by long digestion with concentrated hydrochloric acid, is converted into chloride of lead and volatile products.

The sulphate also appears as a crystalline mass when plumbic-bis-ethyle is gently warmed with a few drops of concentrated sulphuric acid. It is conveniently prepared by agitating the materials in a stoppered bottle, an exit being made from time to time for the gas which is liberated.

Both these salts require analyses to fix their composition, the details of which the author hopes shortly to be able to communicate.

The Action of Zinc-ethyle on Chloride of Silver.

These substances react with some violence, and a black substance sinks in the liquid, which proved to be a mixture of chloride and metallic silver. The zinc-ethyle seems partly to escape decomposition, even when the chloride is in excess and considerable heat is applied. On the addition of water, effervescence sets in, and chloride of zinc is alone found in solution.

In another experiment dry ether was employed instead of water, under a supposition that a solid compound might be formed, soluble in that menstruum. The only reaction, however, appeared to be that expressed by the equation,

$$C_4 H_5 Zn + Ag Cl = Zn Cl + Ag + C_4 H_5.$$

A similar negative result was obtained when zinc-ethyle was made to react on protochloride of platinum, Pt Cl. The action is violent, and the platinum is thrown down in the form of platinum-black.

The same remark also applies to protochloride of copper, $Cu_2 Cl$, when similarly treated; no combination of copper and ethyle could be thereby eliminated.

Action of Zinc-ethyle on Iodide of Stan-ethyle.

This iodide, $C_4 H_5 Sn, I$, was readily obtained by heating sealed tubes containing excess of tinfoil and iodide of ethyle from 150° to 160° C. The pure transparent crystals which were obtained by a

little management, were introduced, in a melted state, into a retort containing zinc-ethyle. It is necessary to cool the apparatus with water. After breaking up the resulting mass, the retort was heated until the thermometer marked 210° C., and the distillate, which contained a slight excess of zinc-ethyle, was agitated with water, and treated with dilute acid, as before described.

The resulting heavy liquid was again distilled, and fractionized with the thermometer. By far the larger portion came over between 170° and 180° as a clear and colourless body, insoluble in water, but soluble, like the other radicals, in ether. That portion which possessed a boiling-point between 176° and 180° C., was taken for examination, and was found, when burned with oxide of copper, to give the formula

$$Sn\,C_8\,H_{10}, \text{ or } Sn\,(C_4\,H_5)_2.$$

This compound, for which the name stannic bis-ethyle is proposed, has a specific gravity of 1·192. In its external and more prominent characters it resembles plumbic bis-ethyle; but an exception may be made, that it is more stable. It is very combustible, burning with a coloured flame and scintillation like that exhibited by the metal tin under the flame of the hydro-oxygen blowpipe.

This radical appears to differ in several particulars from the organo-metal stan-ethyle, $C_4\,H_5\,Sn$, obtained by Dr. Frankland by acting on sheet-zinc with a salt of stan-ethyle. This last body is described as a thick, oily substance, possessed of a powerful odour, and having a specific gravity of 1·55. It differs also in its lower boiling-point, which is about 150° C.

Pure stannic bis-ethyle is perfectly limpid, inodorous, and is acted upon by hydrochloric acid with difficulty. A gas is slowly evolved on the application of heat, and a chloride is formed which seems to be richer in tin than the radical itself.

The chloride appears to crystallize with difficulty, and at usual temperatures has the consistence of an oil. It possesses a powerfully pungent odour, and when heated, a vapour which painfully attacks the skin of the face, and produces fits of sneezing.

A corresponding bromide is formed when bromine is added to stannic bis-ethyle. It is an oily body, with an irritating odour. When acted upon by ammonia, an oxide is precipitated, which with acids forms beautiful crystallizable salts, readily soluble in water.

A complete history of these salts, and their decompositions with zinc-ethyle, will possess much interest, and may prove of value in referring to a few simple radicals the numerous complex bodies described by Löwig, &c.

The author is at present engaged on this branch of the inquiry, a detailed account of which he hopes to embody in a communication to the Royal Society, the present paper being intended only as an outline to be hereafter filled in.

In conclusion, the author would remark that a rich harvest can scarcely fail to be reaped, from submitting to the action of zinc-ethyle the metallic compounds of other groups, such as arsenic, bismuth, and antimony.

THE CHEMICAL GAZETTE.

No. CCCLXXXVI.—November 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Tannine of Galls. By M. KAWALIER.

ROCHLEDER gives the following account of an investigation of the tannine of galls made by Kawalier.

As by treatment with lead-salts Kawalier had been unable to prepare pure tannine, that is to say a substance which furnished no ellagic acid and no sugar when decomposed, he endeavoured to attain his object in another way.

Tannine (prepared by Merk of Darmstadt) was dissolved in the smallest possible quantity of water, and mixed with a little solution of neutral acetate of lead; after continued shaking the precipitate was separated by filtration. On the addition of water the filtrate furnished a precipitate, which was also separated. This last precipitate, when suspended in water and treated with sulphuretted hydrogen, furnished a strongly coloured and extremely impure tannic acid. The fluid filtered from this precipitate was thrown down in three portions by solution of acetate of lead.

By washing with water, suspension in water, decomposition by sulphuretted hydrogen and separation of the sulphuret of lead by filtration, the first of these precipitates furnished a solution, which gave a large quantity of ellagic acid when treated with muriatic acid in the absence of the air, after the sulphuretted hydrogen had been expelled by carbonic acid gas from the hot liquid. This portion of the tannic acid consequently contains a considerable quantity of an impurity.

The second precipitate, after washing with water, was also decomposed by sulphuretted hydrogen under water, and the excess of sulphuretted hydrogen was expelled by carbonic acid gas, after the sulphuret of lead had been removed by filtration.

This solution of tannine was mixed with a solution of tartrate of potash and antimony, and as by this only a turbidity, but no precipitation of the fluid was produced, some carbonate of ammonia was

added, which caused a more abundant precipitate; this was collected upon a filter, washed with hot water, suspended in water, and decomposed by sulphuretted hydrogen. The fluid filtered from the tersulphuret of antimony was freed from sulphuretted hydrogen by heating in a current of carbonic acid gas, and evaporated *in vacuo* over sulphuric acid. After it had been for a short time under the bell-glass, a strong turbidity of the fluid made its appearance; a substance, which acquired a brownish colour when dried, separated from the solution. After this impurity had been removed by filtration, there remained a nearly colourless solution of the tannine of galls, which, when evaporated *in vacuo*, left a colourless, amorphous residue, the aqueous solution of which, when treated with muriatic acid in an atmosphere of hydrogen, furnished no ellagic acid. But besides gallic acid there were produced a small quantity of sugar, and a trace of a brown, pulverulent matter, which, being insoluble, was deposited from the fluid.

The third precipitate with acetate of lead, when washed with water, suspended in water, and decomposed with sulphuretted hydrogen, furnished, after the expulsion of the excess of sulphuretted hydrogen by carbonic acid gas and the removal of the sulphuret of lead, a fluid, which, when treated with muriatic acid in an atmosphere of hydrogen, gave a considerable quantity of ellagic acid. With solution of tartrate of potash and antimony this fluid gave a slightly yellowish, gelatinous precipitate, which stopped up the pores of the filter so that it could not be washed.

The following are some further experiments upon the behaviour of tannine towards strong bases in the absence of air.

A portion of tannine dissolved in little water was partially precipitated by sulphuric acid; the yellowish sticky flakes, which caked together after some time, were removed, and sulphuric acid again added. When the flakes appeared pure white, they were collected, separated from the acid and somewhat coloured mother-liquor, and dissolved in water; the solution was then put into a flask, from which the air was displaced by hydrogen gas. An excess of hydrate of baryta, dissolved in hot water, was then put into the flask without allowing the admission of air. The precipitate of tannate of baryta produced at first, has a slightly yellowish colour, but soon becomes brownish, when the contents of the retort are heated to boiling. After heating for two or three hours no further change was observed. Instead of hydrogen, carbonic acid was passed through the flask; the contents were put upon a filter after they had become cool, the filtered fluid was precipitated with basic acetate of lead, the precipitate removed, the lead contained in the filtrate got rid of by sulphuretted hydrogen, and the sulphuretted hydrogen by heating and carbonic acid. This fluid, when evaporated *in vacuo* over sulphuric acid, leaves a syrupous residue of a strongly acid taste, which dissolves almost completely in alcohol. The small portion insoluble in alcohol leaves a considerable residue when burnt.

The alcoholic solution, separated from the portion insoluble in

alcohol by filtration, was evaporated in the water-bath, dried at 212° F., and analysed. It gave—

C	45·26	24	= 144	45·71
H	6·37	19	19	6·03
O	48·37	19	152	48·26

A solution of this acid in water, neutralized by baryta-water and mixed with absolute alcohol, gives a precipitate in the form of white flakes, which stick together when heated, and solidify on cooling into a brittle mass. When dried at 212° F. the baryta-salt gave 42·51 per cent. of baryta.

The acid and salt are therefore to be regarded as impure glucic acid and glucate of baryta. To obtain the glucic acid pure, fresh portions of tannine were decomposed by baryta in a somewhat different way.

An aqueous solution of tannine was heated to boiling with solution of baryta in an atmosphere of hydrogen; the fluid was separated by filtration from the gallate of baryta after the completion of the decomposition and after it had become perfectly cold; the yellowish filtrate was agitated with air, and the rust-coloured precipitate thus produced removed. The filtrate no longer gives the reaction of gallic acid with persalts of iron. To get rid of the baryta, dilute sulphuric acid was added. The fluid separated from the sulphate of baryta is nearly colourless. For the removal of the sulphuric acid some basic acetate of lead was added, and the sulphate of lead removed by filtration. The fluid was then completely precipitated by neutral acetate of lead, the precipitate was washed and suspended in water, and decomposed by a current of sulphuretted hydrogen gas. The excess of sulphuretted hydrogen was expelled by heat and carbonic acid, and the fluid evaporated *in vacuo* over sulphuric acid. There remained a thick, tenacious, yellowish syrup, of a strong acid taste, which was dried at 212° F., and analysed with the following results:—

	After deduction of the ash.			
C	45·04	16	= 96	45·07
H	6·17	13	13	6·10
O	48·79	13	104	48·83

$$C^{16}H^{13}O^{13} = C^{16}H^{11}O^{11} + 2HO.$$

The aqueous solution of the acid was supersaturated with baryta-water, the excess of baryta removed by carbonic acid gas, and the solution mixed with alcohol. A white flocculent precipitate is formed; it becomes viscid at 212° F., and on cooling again solidifies to a brittle mass, which may easily be reduced to a white powder. The compound contains 44·06 per cent. of baryta.

The formula $C^{16}H^{11}O^{11} + 2BaO$ requires 43·96 per cent. BaO.

The salt is therefore neutral; it agrees in its composition with the lime-salt analysed by Mulder, for which he advanced the formula $2(C^{8}H^{5}O^{5}, CaO) + HO$.

The acid prepared by Kawalier resembles glucic acid in all its reactions and properties, with the exception of a single one. The glucic acid from tannine could not be obtained in a solid form, it was always viscid; whilst the glucic acid from sugar is described as a solid, hard body.

Pure grape-sugar was dissolved in as little water as possible; the solution was put into a flask in which the air is replaced by hydrogen gas, and solution of baryta added in excess. As long as the temperature is kept below the boiling-point, the fluid remains wine-yellow; but as soon as the fluid begins to boil, it becomes brown. As in this experiment all access of oxygen was excluded, it appears therefrom that the formation of brown products of decomposition entirely depends on the temperature. The fluid which distils off during ebullition is colourless. It was saturated with chloride of sodium, and distilled until the distillate was inodorous. This distillate was again saturated with chloride of sodium, and the process repeated several times. In this way a few drops of a fluid were obtained, which proved to be acetone.

The contents of the flask were treated with carbonic acid and the carbonate of baryta removed by filtration. It was coloured, and, when treated with water containing sulphuric acid, gave a brown fluid, from which a brown substance was deposited after standing for some time.

The fluid filtered from the carbonate of baryta was mixed with sulphuric acid, the sulphate of baryta removed by filtration, and the filtrate submitted to distillation. The distillate was colourless and clear, and possessed a strong acid reaction and a strong, peculiar odour, resembling that of fenugreek. This odour is distinctly perceptible in colonial raw sugar. This sweet smelling, acid distillate was mixed with carbonate of baryta, of which it dissolved a considerable quantity with effervescence. The filtered colourless solution was evaporated *in vacuo* over sulphuric acid. A mass of brittle needles, of a very slightly yellowish colour and a faint sweet odour, remained. In water these crystals are very soluble; they are thrown down in the form of a white crystalline powder from the concentrated aqueous solution, on the addition of alcohol. The analysis of the substance dried *in vacuo* gave:—

C	15·93	6 =	36	14·94
H	1·95	4	4	1·66
O	21·24	6	48	19·90
BaO	61·78	2	153·066	63·50

The salt, which was evidently not quite pure, is, to judge from its composition, formacetate of baryta. The sweet smelling acid, however, is by no means a mixture of acetic and formic acids, but a double acid, differing widely from a mixture of the two acids.

As during the treatment of tannine with baryta, without access of air, glucic acid is formed, and traces of formacetic acid may also be detected by the smell, it follows that the hydrate of carbon which makes its appearance together with gallic acid in the decomposition

of impure tannine behaves towards alkalies in the same way as grape-sugar.

The residue of distillation in the preparation of the formacetic acid was made use of to prepare glucic acid. In order to get rid of the small quantity of sulphuric acid contained in the fluid, a drop or two of baryta-water were added; the sulphate of baryta was removed by filtration, and the filtrate precipitated by basic acetate of lead. The precipitate was washed with water, when a considerable quantity of it was dissolved. It was suspended in water, and decomposed by sulphuretted hydrogen; the sulphuret of lead was then removed, the excess of sulphuretted hydrogen driven off, and the solution of the acid evaporated *in vacuo* over sulphuric acid.

In this case also the glucic acid remained in the form of a soft mass, which did not become hard or pulverizable even by drying at 212° F.

These experiments of Kawalier prove that tannine may be obtained free from the impurity which furnishes ellagic acid by treatment with acids. But, according to these experiments, the tannine cannot be entirely purified from the second body which furnishes sugar when decomposed, although the amount of this impurity may be so much reduced that the quantity of sugar may only be 4 per cent. of the weight of tannine employed for the decomposition.

These experiments confirm the results of W. Knop, who converted the whole of the tannine into gallic acid, except a loss of 4—6 per cent., which consisted of ellagic acid and a hydrate of carbon. These small quantities of sugar show distinctly that tannine cannot be arranged in that class of bodies to which we refer salicine, amygdaline, æsculine, phloridzine, &c.

We should have to assume that in the decomposition of tannine at least 11 equivs. of gallic acid are produced for 1 equiv. of sugar. Nothing remains, therefore, but to state that tannine and gallic acid stand in the same or in a very similar relation to each other as dextrine and grape-sugar; that pure tannine is converted into gallic acid by the reception of the elements of water, when it is exposed for a time to a high temperature with acids or alkalies without access of air; and that the small quantities of sugar which are thus produced, arise from impurities, which have not yet been successfully got rid of.

To get at the true nature of tannine, it will be especially necessary to find the means of preparing it free from all impurities, and to study the nature of gallic acid, which is almost unknown. Whether gallic acid is an acid or an aldehyde, and many questions of the same kind, are still unanswered. Whether the formula of tannine contains 14 equivs. of carbon, or 28, or 42, &c., cannot be seen from the experiments hitherto made, but there is no doubt that both Strecker's old and new formulæ are incorrect, and that the carbon of tannine is neither 40 nor 54 equivs., but 42 or 56, if the atomic weight of tannine be really so high.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxx. p. 159.

Note on the Benzoic Derivatives of Quinine, Cinchonine, and Strychnine. By M. SCHUTZENBERGER.

Dry cinchonine treated with chloride of benzoyle dissolves with elevation of temperature. If the mixture is heated for a few moments, it very quickly produces a crystalline mass of monochlorhydrate of benzoyle-cinchonine formed according to the equation

$$C^{40}H^{24}N^{2}O^{2} + C^{14}H^{5}O^{2}Cl = C^{40}H^{23}(C^{14}H^{5}O^{2})N^{2}O^{2}ClH.$$

The product dissolves readily in water; the chloride of benzoyle in excess remains at the bottom of the liquid. By decanting before the latter can decompose and saturating the solution with ammonia, a white resinous precipitate is formed, which coheres into a solid, soft, and tenacious mass, hardening after complete cooling. The new substance thus obtained is basic, and represents the cinchonine with one equivalent of hydrogen replaced by benzoyle. The capacity for saturation of the cinchonine is not altered by this substitution, as will be seen in the sequel. The benzoyle-cinchonine is soluble in all proportions in alcohol and æther, insoluble in water, tasteless and uncrystallizable. It fuses on a strip of platinum, and burns, becoming partly volatilized. Heated with soda-lime it gives off benzine. Dried at 302° F. it gave

		Calculated.
Carbon	78·47	78·64
Hydrogen..	6·98	6·79

leading to the formula $C^{40}H^{23}(C^{14}H^{5}O^{2})N^{2}O^{2}$.

Chloroplatinate of benzoyle-cinchonine analysed after being dried at 284° F., and the same chloroplatinate incinerated, gave—

		Calculated.
Carbon	38·97	39·27
Hydrogen..	3·84	3·63
Platinum ..	23·94	24·00

leading to the formula $C^{40}H^{23}(C^{14}H^{5}O^{2})N^{2}O^{2}2(ClH, Cl^{2}Pt)$.

The salts of this alkaloid are very soluble in water.

Quinine dried at 266° F. likewise dissolves with evolution of heat in chloride of benzoyle. After cooling, the mass presents the appearance of a thick syrup formed of a mixture of monochlorhydrate of benzoyle-quinine and chloride of benzoyle. Water dissolves the first product very readily. Ammonia precipitates the base in the form of a colourless resinous mass, presenting the same characters as benzoyle-cinchonine. Chlorine and ammonia develope the green coloration of quinine.

In the resinous state it contains, like its cinchonic analogue, much water eliminable at 284° F. Dried at 284° it gave—

		Calculated.
Carbon	75·76	75·7
Hydrogen..	6·76	6·5

The formula is therefore $C^{40}H^{23}(C^{14}H^{5}O^{2})N^{2}O^{4}$.

The chloroplatinate gave on incineration,—

		Calculated.
Platinum ..	23·2	23·5

Formula:—$C^{40}H^{23}(C^{14}H^{5}O^{2})N^{2}O^{4}2(ClH, Cl^{2}Pt)$.

Under the same circumstances strychnine gave a neutral derivative, only half of the base being modified, the other half combining with the hydrochloric acid produced during the reaction.

$$2(C^{42}H^{22}N^{2}O^{4})+C^{14}H^{5}O^{2}Cl=C^{42}H^{22}N^{2}O^{4}, ClH$$
$$+C^{42}H^{21}(C^{14}H^{5}O^{2})N^{2}O^{4}.$$

The benzostrychnide is solid, colourless, very slightly soluble in water, very soluble in alcohol and æther, slightly bitter, insoluble in acids. It softens below 212°, and fuses a little above into a resinous mass which crystallizes on cooling.

By the action of chloride of acetyle upon quinine and cinchonine, I have likewise obtained acetylic derivatives, playing the part of base, and with the capacity for saturation unchanged; they are represented by $C^{40}H^{23}(C^{4}H^{3}O^{2})N^{2}O^{4}$ or O^{2}, and affect the form of semifluid resins, of a burning taste, but not bitter.

These reactions apply to all the alkaloids, and will be generalized in a forthcoming paper.

The complete analysis of a quinine, of its chloroplatinate and its benzoic derivative, lead me to suppose the existence of a variety of this base nearly related by its properties to ordinary quinine, but corresponding to the formula

$$C^{40}H^{26}N^{2}O^{4},$$

instead of

$$C^{40}H^{24}N^{2}O^{4}.$$

This base, precipitated from an acid solution by ammonia, changes after some hours, in the liquid in which it has been precipitated, into fine tufts formed of longish needles, while ordinary quinine only gives very small needles. Another quinine yielded me tufts formed of flat lamellæ, but the quantity was too small for analysis. When ammonia is added to a dilute solution of hydrochlorate of strychnine free from bromine, the liquid becomes filled in about half a minute with very long and slender needles; the separated water deposits in about a quarter of an hour small octahedra. The needles are ordinary strychnine, C^{42}, the octahedra strychnine, C^{40}. This very clear separation bears out what I have already announced as to the different varieties of this base.—*Comptes Rendus*, August 2, 1858, p. 233.

On the Synthesis of the Hydrocarbons. *By* M. Berthelot.

[Continued from page 404.]

Hitherto the carburets of hydrogen have always been formed by the destruction of pre-existing compounds. By means of this destruction, usually effected by the agency of heat, the elements of the compound divide into two unequal portions; one portion of its

carbon and of its hydrogen burn completely at the expense of its oxygen, whilst the other portion of the elements separates under the form of principles more combustible than the original material. These principles are generally more simple, not only in their composition, but also in the number of equivalents of carbon which their formula includes.

But this process is purely analytical; it does not allow us to get over the first step of the synthesis, for it presupposes the existence of compounds of carbon with hydrogen.

This is easily seen by considering the processes by which chemists prepare the hydrocarbons.

Thus marsh-gas, $C^2 H^4$, was first extracted from the products of the spontaneous decomposition of vegetable remains, and then formed by decomposing organic substances, and especially the acetates by heat.

Olefiant gas, $C^4 H^4$, formed in the dry distillation of a great many organic matters, is generally prepared with ordinary alcohol, a product of the fermentation of sugar.

Propylene, $C^6 H^6$, butylene, $C^8 H^8$, amylene, $C^{10} H^{10}$, and the analogous carburets, are prepared either by means of the corresponding alcohols, or by the dry distillation of a great number of salts, all more complicated than the resulting carburets.

All these carburets belong to a single series which starts from olefiant gas; all contain carbon and hydrogen in equal equivalents, but more and more condensed.

Naphthaline, $C^{20} H^8$, and benzine, $C^{12} H^6$, do not belong to this series; but, like the preceding carburets, they are only prepared from organic compounds.

In all cases the formation of the carburets of hydrogen has hitherto been the result of an analytical process, of a decomposition in virtue of which the elements of a complex substance group themselves into more simple compounds.

The investigations which I have carried on proceed in a precisely opposite manner, and realize the synthesis of the hydrocarbons and of the alcohols.

Thus, marsh-gas, $C^2 H^4$, may be formed by the distillation of formiate of baryta which has been produced with oxide of carbon extracted from carbonate of baryta. Marsh-gas may also be produced by means of sulphuret of carbon.

Olefiant gas, $C^4 H^4$, has been formed in the distillation of formiate of baryta, itself produced with oxide of carbon extracted from carbonate of baryta. Olefiant gas has also been obtained by means of sulphuret of carbon.

Propylene, $C^6 H^6$, has been formed in the distillation of formiate of baryta, itself produced with oxide of carbon extracted from carbonate of baryta.

Butylene, $C^8 H^8$, and amylene, $C^{10} H^{10}$, have been formed in the distillation of acetate of soda, derived from alcohol, which in turn may be formed by means of the olefiant gas prepared by the preceding processes.

Naphthaline, $C^{20}H^{8}$, has been formed by means of sulphuret of carbon, alcohol, and acetic acid.

Benzine, $C^{12}H^{6}$, has been formed by means of alcohol, and by means of acetic acid, which may be produced with olefiant gas.

The starting-point of the synthesis of organic compounds is therefore ascertained; it only remains to ascend from the hydrocarbons to the oxygenated compounds, that is to say, to reverse the ordinary conditions of the production of these same carburets. This has been realized by the conversion of the hydrocarbons into the corresponding alcohols.

Hitherto the various alcohols had been produced in various ways by means of compounds more complicated than themselves, and without being related to these compounds by any general and regular relation.

Thus methylic alcohol, or wood-spirit, $C^{2}H^{4}O^{2}$, had been met with amongst the numerous products of the distillation of wood, that is to say, a totality of organized vegetable substances.

Ordinary alcohol, $C^{4}H^{6}O^{2}$, is a normal and regular product of the fermentation of sugar; its sole origin was therefore drawn from a proximate principle extracted from the vegetable kingdom, and which could not be formed.

Amylic alcohol, $C^{10}H^{12}O^{2}$, butylic alcohol, $C^{8}H^{10}O^{2}$, propylic alcohol, $C^{6}H^{8}O^{2}$, were accessory, if not accidental products of fermentation.

Caprylic alcohol, $C^{16}H^{18}O^{2}$, was formed in the distillation of castor oil in presence of alkalies.

Æthalic alcohol, $C^{32}H^{34}O^{2}$, and cerylic and melissic alcohols had been formed by means of spermacetic, and of certain waxes, produced by the combination of fatty acids with these alcohols.

For these various processes, which are all analytic, the author has substituted a set of direct and regular methods, which permit the synthetic formation of the alcohols by means of the hydrocarbons.

Thus methylic alcohol, $C^{2}H^{4}O^{2}$, is formed with marsh-gas, $C^{2}H^{4}$, by replacing 1 equiv. of hydrogen by chlorine, $C^{2}H^{3}Cl$, and decomposing the methylohydrochloric æther thus formed by potash.

Ordinary alcohol, $C^{4}H^{6}O^{2}$, and propylic alcohol, $C^{6}H^{8}O^{2}$, have been formed by combining olefiant gas, $C^{4}H^{4}$, and propylene, $C^{6}H^{6}$, with sulphuric acid, and then decomposing this compound by water; the elements of water remain combined with the hydrocarbon.

Lastly, propylic alcohol, $C^{6}H^{8}O^{2}$, amylic alcohol, $C^{10}H^{12}O^{2}$, caprylic alcohol, $C^{16}H^{18}O^{2}$, æthalic alcohol, $C^{32}H^{34}O^{2}$, and probably all the others may be obtained by means of their hydrochloric, hydriodic, or hydrobromic æthers, $C^{6}H^{7}Br$, $C^{10}H^{11}Br$, $C^{16}H^{17}Br$, $C^{32}H^{33}Br$, which are produced by the direct union of the hydracid with the corresponding hydrocarbons, propylene, $C^{6}H^{6}$, amylene, $C^{10}H^{10}$, caprylene, $C^{16}H^{16}$, æthylene, $C^{32}H^{32}$, &c.

We may therefore realize the complete synthesis of all the alcohols whose hydrocarbons have been produced by means of the corresponding simple bodies, that is to say, methylic, vinic, propylic, butylic, amylic alcohols, &c. Now, from the labours of modern

chemists, these alcohols have become the starting-point of most of the other organic compounds.

To realize the complete synthesis of the hydrocarbons and alcohols, is therefore to realize the synthesis of an almost infinite number of organic compounds, both natural and artificial, by means of the simple bodies of which they are composed.—*Comptes Rendus*, June 14, 1858, p. 1161.

On the Artificial Formation of Oxychloride of Copper (Atacamite) and the Sulphates of Copper. *By* FREDERICK FIELD, F.R.S.E.*

Oxide of copper and other matters carried over by the draught from some copper smelting furnaces were deposited for more than six months in the culvert or underground chimney leading to the principal stack. The bottom or floor of the culvert was not bricked, but consisted simply of the soil, underneath which were some salt springs from which water strongly impregnated with saline material continually rose. The chimney was built close to the margin of the sea, and before the furnaces were lighted the horizontal floor was always very damp. Layers of some inches in thickness of the metallic dust had been deposited, and when the chimney was opened, bright green and blue strata were observed, underlying the brownish earthy-looking substance which was constantly exposed to the flame from the furnaces. Although the culvert had been at a full red heat for many months, the salts on the floor contained much water, many specimens being beautifully crystallized, having been protected from the flame by the continual deposition of fresh powder, and doubtless owing their formation to the action of the saline substances oozing up from below, upon oxide of copper at a comparatively high temperature.

An analysis of one very clean specimen of the blue variety gave the following results:—34·50 per cent. was soluble in water, and with the exception of traces of chlorine, gave simply sulphuric acid and oxide of copper, evidently being the ordinary sulphate. The remaining 65·50 dissolved easily in dilute nitric acid, after having been dried at a temperature of 212°, and gave 47·20 oxide of copper, and 18·21 sulphuric acid, corresponding very closely to the formula of a basic sulphate of the composition $3CuO, SO^3$.

Other specimens had a grass-green colour, and were highly deliquescent, appearing to be mixtures of the ordinary and basic sulphates, the former partially dehydrated, and regaining its water from the air. From the rapid absorption of moisture, the analysis was very difficult, but the soluble portion, amounting to about 40 per cent., gave equal weights of sulphuric acid and oxide of copper, and the residue proved to be highly basic.

But by far the greater portion of the deposit in the chimney consisted of oxychloride of copper, having exactly the appearance, properties, and composition of the native mineral:—

* Communicated by the Author.

Atacamite.—100 grains yielded:—

Copper.....	56·92
Chlorine	16·30
Water	16·14

or,

Oxide of copper	53·11
Chloride of copper ..	30·73
Water	16·14

or, $3CuO, CuCl+4HO$,

with traces of iron and sulphuric acid.

Native atacamite gives—

Copper.....	57·13
Chlorine	16·07
Water	16·07

The oxychloride was perfectly insoluble in water, and thus could be easily separated from the soluble chlorides and sulphates which existed in small quantities. It was entirely soluble in ammonia. More than eight tons of oxychloride, and from four to five of the sulphates, were obtained.

It appears from this that oxide of copper in the presence of the alkaline chlorides and sulphates at an elevated temperature, becomes entirely converted into sulphate and oxychloride. The upper stratum of the deposit consisted chiefly of oxide of copper; immediately underneath this anhydrous oxychloride, with basic sulphate, and on the floor of the chimney, hydrated oxychloride with the crystallized sulphate as well as the basic salt.

Coquimbo, Chile, Sept. 15, 1858.

ANALYTICAL CHEMISTRY.

Note on the Drying and Weighing of Precipitates in Chemical Analyses. By C. MÈNE.

ONE of the greatest troubles and difficulties in chemical analyses is the drying of the precipitates destined by weighing to furnish the numerical result of the composition of the substances under examination. Hence chemists have readily adopted the employment of standard solutions, which usually combine promptitude and precision. There are, however, circumstances in which this mode of operation is impracticable, and then it is necessary to have recourse to a series of long, and often defective operations. In industrial laboratories especially the methods of analysis generally indicated in books are far too tedious for adoption, and they are nearly always replaced by approximative results.

The method proposed by the author consists in washing the precipitate carefully by decantation, and introducing it, with water, into a specific gravity bottle. The difference of the weight of the bottle filled with pure water and with water containing the precipitate gives the desired result.

When water might have an injurious effect upon the precipitate, he replaces it by another fluid; thus he employs alcohol in place of pure water in the determination of chloride of sodium, sulphate of lime, ammonio-chloride of platinum, &c.—*Comptes Rendus*, June 28, 1858, p. 1268.

Process for the Estimation of Urea by the Hypochlorite of Soda. *By* M. LECONTE.

My method consists in oxidizing urea by the aid of hypochlorite of soda, from which reaction results carbonic acid, water, nitrogen, and chloride of sodium, as appears from the following formula:—

$$C^2 H^4 N^2 O^2 + 6(NaO, ClO) = 6NaCl + 4CO^2 + 6HO + 2N.$$

This reaction commences in the cold, but it becomes more energetic, and especially commences more promptly, with the aid of a gentle heat; the gases are evolved with perfect regularity during the whole course of the experiment, which lasts about half an hour.

It struck me it might be possible to estimate the urea by determining chlorimetrically the quantity of chlorine which disappeared during the reaction; experiment proved that it was infinitely more exact to collect the nitrogen evolved, all the carbonic acid produced being retained in the liquid in the state of sesquicarbonate of soda, undecomposable by heat.

The nitrogen thus obtained, in spite of its odour of chlorine, does not diminish in volume when agitated with solution of potash, nor with alkaline solution of pyrogallic acid, which indicates the absence of carbonic acid and oxygen, and demonstrates that the quantity of chlorine, to which the nitrogen owes its odour, is altogether insignificant.

The apparatus I employ is composed of a bottle or a little flask of 150 cubic centims. capacity, furnished with a tube for collecting the gas, which has its end adjusted under a graduated tube filled with water.

The preparation of the hypochlorite consists in methodically exhausting 100 grms. of well-powdered hypochlorite of lime with boiling and cold water, dissolving in the filtered liquid 200 grms. of crystallized carbonate of soda reduced to fine powder, filtering and washing the carbonate of lime, and uniting the liquids, which are made up to 2 litres.

In making an analysis, the urea is placed in the flask with a little water, the hypochlorite quickly added, to completely filling the bottle, so that when the cork is placed in it, a little of the liquid rises into the tube, which should be of small diameter; when this column of liquid has arrived at the end of the gas-tube, the latter is adjusted under the graduated tube; the flask is then placed in a little water-bath and heated slowly to ebullition. When, notwithstanding this temperature, the gas is not evolved in any quantity, it must be heated directly by the spirit-lamp, and the ebullition con-

tinued until the vapour produces a sharp noise in condensing in the water, which indicates that it contains no more gas.

The urine must be previously purified in the following manner:—to 20 grms. of urine are added 3 grms. of subacetate of lead in solution; it is boiled, filtered, and the filter three times washed; 3 grms. of powdered carbonate of soda are then added; it is boiled again, again filtered, and washed three times; the liquid obtained, ordinarily forming 50 cubic centims., is measured, and one-half, representing 10 cubic centims. of urine, is heated as above.

Although theory indicates that 1 decigrm. of urea should furnish 37 cubic centims. of nitrogen, I could never obtain more than 34 cubic centims.; but this number was constant, as is shown by the subjoined Table; by dividing the volume of nitrogen therefore, after correction, by 34, we obtain within a few thousandths the weight of the urea.

It is evident on comparing the last two experiments on the list, that the other nitrogenous matters of urine furnish an amount of nitrogen infinitely smaller than that of the urea; and that in the present case the proportion is :: 54 : 1000; consequently my process enables us not only to ascertain the variations in the amount of the urea, but also those of the azotized substances accompanying it.

Table giving a summary of experiments made to verify the foregoing process.

Experiments.	Urea employed.	Nitrogen obtained in centims.	Temperatures, F.	Pressure.	Tension of the vapour of water.	Nitrogen corrected.	Urea found.	Difference for 1.
	grm.		°			cubic centims.	grm.	
1.	0·060	22	64·4	759·75	15·35	20·44	0·0601	0·0018
2.	0·0575	22·25	75·2	755·15	22·21	19·71	0·0579	0·007
3.	0·050	18·4	57	755·15	12·67	16·86	0·0502	0·004
4.	0·050	18·3	57	755·15	12·67	17·09	0·502	0·004
5.	0·100	38·25	64·4	757·75	15·35	34·94	0·102	0·020
6.	0·100	36·2	60·8	763·4	13·52	34·17	0·1005	0·005
7.	0·100	37	65·1	757·2	15·35	33·38	0·0982	0·018
8.	0·100	36	71·6	761	dry gas	33·76	0·0993	0·007
9.	0·115	42·2	62·6	761	14·41	39·28	0·1155	0·004
								Urea for 1000
10.	10 c. c. urine	36·2	60·8	757·75	13·52	33·49	0·0985	9·85
11.	10 c. c. of the same	37·25	60·8	757·75	13·52	33·45	0·984	9·84
12.	12·25 c. c. do.	44·4	60·8	757·75	13·52	41·07	0·1207	9·85
13.	10 c. c. different	39·8	69	764·7	17·4	32·38	0·0952	9·52
14.	10 c. c. purified	37·6	69	764·7	17·4	30·61	0·0900	9·90

Comptes Rendus, August 2, 1858, p. 237.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 17, 1858. (The Lord Wrottesley, President, in the Chair.)

"Contributions towards the History of the Monamines." By A. W. Hofmann, Ph.D., F.R.S.

The progress of my experiments on the poly-ammonias and on the phosphorus-bases, now and then involves the study of reactions which are scarcely comprised between the boundary lines of the principal inquiries. For the sake of perspicuity, I beg leave to submit the results of these studies separately to the Society.

1. *Action of Bibromide of Ethylene on Trimethylamine.*

The unexpected result obtained in the action of bibromide of ethylene on triethylphosphine, induced me to examine the deportment of the tertiary amine-bases under the influence of the same agent. As a characteristic representative of this class I have selected trimethylamine, which may be readily procured in tolerable quantity and in a state of purity.

On submitting trimethylamine to the action of bibromide of ethylene, phenomena are observed which are perfectly similar to those which occur in the analogous experiment with triethylphosphine. On account of the volatility of the trimethylamine, I have never worked with the anhydrous base, but invariably either with aqueous or alcoholic solutions. At the common temperature bibromide of ethylene is only gradually acted on by an aqueous solution of trimethylamine. Frequent agitation and contact for several days are necessary to complete the reaction; addition of alcohol accelerates the process; which may be still very considerably shortened by exposure of the mixture in sealed vessels to a temperature of from 40° to 50°. To exclude complication, it is desirable to avoid a higher temperature and to keep always the bromide in considerable excess.

By adopting these precautions, the mixture of the two bodies is soon found to deposit a white crystalline salt, the formation of which continues until the liquid has assumed an acid reaction. A considerable quantity of this salt is dissolved in the water; it is therefore most convenient to distil off the excess of bibromide of ethylene and to evaporate the residuary liquid to dryness. The dry saline mass, separated from a slightly yellowish deliquescent substance by washing with absolute alcohol and once or twice recrystallized from the same solvent, furnishes magnificent white needles, extremely soluble in water, readily soluble in boiling alcohol, much less so in cold alcohol, and insoluble in ether. This salt can be boiled with the fixed alkalies without disengaging a trace of an alkaline vapour. This deportment renders it easy to recognize the absence of impurities.

The composition of this substance, established by many deter-

minations, is represented by the formula

$$C_{10}H_{12}NBr_2 = \left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ (C_4H_4Br)' \end{matrix}\right\} N, Br.$$

This substance, which presents itself as bromide of trimethyl-bromethylene-ammonium, is formed by the simple union of 1 equivalent of bibromide of ethylene with 1 equivalent of the tertiary monamine. A glance at the formula exhibits the perfect analogy of the composition of this compound with that of the bromide formed by the action of bibromide of ethylene on triethylphosphine. The deportment of the two salts with nitrate and with oxide of silver is also similar in every respect.

By treatment with nitrate of silver, the bromine not belonging to the ammonium may be removed without affecting the bromine of the radical. The nitrate thus obtained, after separation of the excess of silver, furnishes with bichloride of platinum a difficultly soluble octahedral salt, crystallizable from a large quantity of boiling water, and containing

$$C_{10}H_{12}BrNCl, PtCl_2 = \left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ (C_4H_4Br)' \end{matrix}\right\} NCl, PtCl_2;$$

and with terchloride of gold an analogous compound crystallizing from boiling water in splendid golden-yellow needles,

$$C_{10}H_{12}BrNCl, AuCl_3 = \left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ (C_4H_4Br)' \end{matrix}\right\} NCl, AuCl_3.$$

Treatment with oxide of silver converts the bromide of trimethyl-bromethylene-ammonium into the oxide of trimethyl-vinyl-ammonium:

$$\left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ (C_4H_4Br)' \end{matrix}\right\} NBr + 2AgO = 2AgBr + \left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_4H_3 \end{matrix}\right\} NO, HO.$$

The solution of this substance is a powerfully alkaline liquid, which, on saturation with hydrobromic acid, furnishes a deliquescent bromide of extreme solubility, entirely differing from the original bromide. The corresponding chloride forms with bichloride of platinum an octahedral salt, likewise extremely soluble in water, but insoluble in alcohol; with terchloride of gold, beautiful yellow needles recrystallizable from boiling water.

Platinum-salt $C_{10}H_{12}NCl, PtCl_2 = \left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_4H_3 \end{matrix}\right\} NCl, PtCl_2.$

Gold-salt .. $C_{10}H_{12}NCl, AuCl_3 = \left.\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_2H_3 \\ C_4H_3 \end{matrix}\right\} NCl, AuCl_3.$

As might have been expected from the experience gathered in the phosphorus-series, the formation of the brominated bromide is invariably accompanied by the simultaneous production of the vinyl-compound, and of a corresponding quantity of hydrobromate of trimethylamine.

$$2\left[\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N + C_4H_4Br_2 = \left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\H\end{matrix}\right\}NBr + \left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_4H_3\end{matrix}\right\}NBr.$$

Indeed it would appear that at a high temperature and with an excess of trimethylamine, the equation just given represents the principal phase of the reaction. In an experiment made under the stated conditions, the liquid in the digester had assumed a deep yellowish colour; and on evaporation and appropriate treatment a crystalline salt was obtained, which on analysis was found to consist exclusively of

$$C_{10}H_{12}NBr = \left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_4H_3\end{matrix}\right\}NBr,$$

the mother-liquor containing a large quantity of hydrobromate of trimethylamine. It is possible that even in this reaction the vinyl-compound was only a secondary product, formed by the decomposition of the brominated bromide under the influence of an excess of trimethylamine.

$$\left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\(C_4H_4Br)'\end{matrix}\right\}NBr + \left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N = \left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\H\end{matrix}\right\}NBr + \left.\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\\C_4H_3\end{matrix}\right\}NBr.$$

Exactly as in the phosphorus-series, together with the compounds described, some other substances are formed, particularly when the process is supported by the action of heat. As yet I do not sufficiently understand these additional reactions.

I have established experimentally that triethylamine and triamylamine, when treated with bibromide of ethylene, give rise to similar reactions. I have not, however, minutely examined the substances which are formed. They are sufficiently characterized by theory.

The unexpected deportment of bibromide of ethylene with the tertiary monamines and monophosphines, furnishes a new proof of the fact, that all our rational formulæ are, after all, the expressions of special reactions. With the alkalies, the brominated Dutch liquid behaves as a double salt of two monatomic compounds,

$$(C_4H_3)'Br + HBr.$$

With silver-salts, with aniline, &c., it exhibits the deportment of a true biatomic compound,

$$(C_4H_3)''Br_2.$$

With the tertiary amines and phosphines, lastly, we find that the elements of the same body, in accordance with the requirement of the case, arrange themselves into one monatomic compound, the

constitution of which, if we simply consider the function which it performs under these special circumstances, might be represented by the formula

$$(C_4 H_4 Br)' Br.$$

It is obvious that the three formulæ,

$$(C_4 H_3)' Br, H Br,$$
$$(C_4 H_4)'' Br_2 \quad \text{and}$$
$$(C_4 H_4 Br)' Br,$$

represent the constitution of this body with reference to certain special conditions; the absolute arrangement of the molecules we ignore altogether, and it is doubtful whether it will ever be accessible to experiment.

"Preliminary Notice of Additional Researches on the Cinchona Alkaloids."—Part III. By W. Bird Herapath, M.D.

Having had occasion to make some experiments upon the rotatory power of the β-quinidine mentioned in the first part of his paper*, he arrived at the conclusion that some other feebly dextro-gyrate alkaloid accompanied it, and of a more soluble and less crystallizable character. Consequently, on its further purification by frequent recrystallization from alcohol, the quinidine was obtained perfectly pure; it then had the molecular rotation assigned to it by Pasteur, namely 250°·75↗. Two examinations have given the following elements:—

I. Its solution having been made in rectified spirit of ·836 by boiling, and crystallized at 62° F., the concentrated solution decanted gave the following elements for Biot's formula:—

ϵ.	δ.	l.	Arc blue violet.	
·02728	·85172	315·8	18°·5↗ =	251°·7↗

II. Its sulphate, perfectly neutral, and concentrated at 61° F.:—

ϵ.	δ.	l.	Arc.	
·0088441	1·00406	315·8	7°↗ =	249°·55↗

These observations were all made with the naked eye, and the tint of passage was that of the blue-violet petal. When the pink violet, or lilac tint was employed, the arc observed was 20°·25 for No. I. experiment, which with the same elements of calculation gave 274°·093↗; and with No. II., the arc 25°·75, which, as before, gave 279°·7↗. The slightly dextro-gyrate alkaloid existing as a contamination was quinicine; and upon its removal, the β-quinidine had the same solubility in ether as the quinidine of Pasteur. One very peculiar circumstance elicited during this examination, was the fact that the perfectly pure recrystallized quinidine, if made into the neutral sulphate and crystallized by cooling, produces, if made with distilled water at 212° F., a slightly greenish solution, however great the care which might have been taken to remove all the mother-water by washing the crystal on the filter. This green tint deepens consider-

* See pp. 56, 70 of the present volume.

ably during concentration, or by boiling, and at length gives rise to the erroneous impression that some salt of copper is present: in this condition, a tube having a length of 315·8 millims., when filled with the solution, is absolutely impervious to light. It is probable that some molecular change is produced by the action of boiling, even if only for a short time; therefore it was necessary to make a concentrated solution at 120° F., and set in repose for some days at 62° F., by which precaution the solution experienced only a very slight discoloration. When formerly experimenting on β-quinidine, the author obtained an iodo-sulphate very different from that which he has described as indicative of the quinidine of Pasteur: having pursued this inquiry, he is now enabled to state that his former discrepancies arose from the fact that quinidine forms two iodo-sulphates, according to the manner in which it is treated.

1st. When a dilute solution of the acid sulphate of quinidine is mixed with one-third or one-half its bulk of rectified spirit and raised to 160° or 180°, then treated with tincture of iodine in small quantities, the red iodo-sulphate is produced, having the characters previously described as indicative of quinidine,—quinine, when similarly treated, invariably producing the optical salt.

The only precaution necessary to be taken in the case of the alkaloid quinidine is to avoid adding an excess of iodine; otherwise an amorphous resinoid substance is deposited which will not crystallize.

2ndly. But when we treat the acid sulphate of quinidine in a concentrated form, diluted with from thirty to forty times its bulk of rectified spirit at a temperature rather below 120° F., with the tincture of iodine, even in greater proportions, an optical salt of quinidine is produced, being the perfect analogue of the quinine salt.

It crystallizes from this strong spirituous solution in acicular long lanceolate prisms, the form of which appears to be a rhomboid having 30° for the acute and 150° as the obtuse angles; but they are more frequently found with a termination like the blade of an ordinary bleeding-lancet. These prisms have a frequent disposition to hemitropism, but in superposition, so that two plates may be often found *overlying each other in a parallel position*, wholly obstructing light in those portions *where they cover each other*, but transmitting an olive- or yellowish-green tint where separate.

Sometimes the terminal planes are rectangular. This imbricated mode of crystallization is very peculiar; and although the author has made thousands of experiments with quinine, yet he never saw anything similar to it; for this alkaloid invariably crystallizes from *dilute alcoholic* solutions as the α-prism, obstructing light when the length is perpendicular to the plane of reflected light polarized in a vertical plane,—or from *strong* alcoholic solutions, where the spirit is about two-thirds the bulk, as β-prisms, which obstruct light in the opposite plane, or, as the author has described it, when the planes of their length "lie in a plane parallel to that of the polarized beam with which they are examined." In the case of quinine, these two sets of prisms never occur together; but if made by separate operations

and then artificially mixed on the same slide, they present the optical characters of this new quinidine salt, viz. *obstructing light when two long prisms overlie each other in a parallel position.* They are therefore α- and β-prisms crystallizing together from the *same strong* alcoholic solution.

The more frequent form in which this salt shows itself, however, is as the α-prism, from solutions in which the alcohol is vastly predominant over the water; whereas with quinine, β-prisms always develope themselves under similar circumstances.

This new quinidine salt has a very great similarity in its optical property to the quinine salt. Its reflected tint is a metallic blue-green, when in liquid or in contact with glass; but after filtering, and when exposed on paper, it has a brownish-olive colour, and loses all appearance of metallic reflexion to the naked eye. Its transmitted tint is, when polarized parallel to its axis, a brownish-yellow green, even in thin plates, but verging to brown in thicker. Its "indicative body-colour" is brownish red.

One great peculiarity attends upon this salt; if it be permitted to remain in the acid mother-liquid, it disintegrates by gradual solution, and disappears, whilst, upon the side of the bottle, solid and large crystals slowly form, of a rhombohedric form, or having some of its modifications, the more frequent of which is that with replacement upon the short axis of the rhombohedron by triangular planes. These crystals have a deep sienna-brown colour by transmission, and a dark steel-blue by reflexion, verging on purple; they strongly polarize light, and differ materially from the garnet-red iodo-sulphate previously described, by the greater intensity of their optical properties.

When we attempt to purify the optical thin prisms by recrystallization from alcohol, the same modification appears to be produced; but the crystals are acicular rhombic prisms; the optical characters are the same, however, as those of the rhombohedral form.

The characters, therefore, by which this salt is known from quinine are many.

1st. Its crystallizing as α-prisms, or as α- and β-prisms from strong spirituous solutions.

2nd. Its brownish-olive reflected tint as seen by the naked eye.

3rd. Its deeper yellow and brownish-green transmitted tint.

4th. The probable difference in the primary form of the laminated variety, being a very acute prism of a rhombic form, having 30° as the acute, and 150° as the obtuse angles.

5th. The modification which it undergoes by resolution or recrystallization, and the formation of a salt more resembling the garnet-red iodo-sulphate, but having strongly marked differential characters from this beautiful salt, viz. its strong tourmaline powers of absorption and its deeper colour, being nearly a brown-purple, and by its disposition to assume the rhombohedric form.

The author has not yet analysed this salt, but hopes ere long to accomplish this matter and communicate his results to the Royal Society; but he ventures to hope that it will be found to contain

2 atoms sulphuric acid and 3 atoms iodine, like the analogous quinine and cinchonidine salts.

The author has also assured himself that there is an analogous class of salts produced by ethyle-quinine and ethyle-quinidine, but optically distinct from those of quinine and quinidine. He has already produced three salts from ethyle-quinine, having optical characters different from any previously described.

1st. A deep purple-red salt by transmitted light, in thicker plates or aciculæ quite impervious to light. This salt occurs as very slender acicular prisms; it has a brilliant metallic-green reflected tint, but very little double absorption.

2nd. There is a foliaceous salt, having a plate-like form, a deep red or orange-red colour, transmitting an orange-yellow, having only slight optical powers.

3rd. A salt having many of the characters of the new quinidine salt when first produced, viz. the optical characters and the α-form; but on attempting to recrystallize it, the orange-red plates just described are alone produced.

The only salt yet produced from ethyle-quinidine is one very similar to the red salt described above, but it has only been very partially examined. The iodide ethyle-quinidine is a very beautiful silky salt, less soluble than the iodide ethyle-quinine. The author is not aware that it has yet been described. It is readily made by mixing an alcoholic solution of quinidine with an etherial solution of iodide-ethyle; on repose, the new iodide ethyle-quinidine separates in long, slender, silky aciculæ; and further crops can be repeatedly produced by diluting the original solution with water until precipitation *begins* to follow; on long repose, the iodide crystallizes and may be removed by filtration, and washed with dilute spirit.

Note.—In reference to the rotatory power of the cinchona alkaloids, the calculation of the molecular rotation gives an excellent plan of deciding on *the purity* of the alkaloid employed; for if the absolute molecular rotation be obtained precisely identical with those given by other optical chemists, the purity may be inferred as proved. But it is possible for a large quantity of two alkaloids to be present in solution, one dextro-, the other levo-gyrate, and in such proportions that the polariscope shall give no indication of the presence of either.

Thus a highly concentrated solution of the acid sulphate of quinine, marking a left-handed rotation of 57°↖, was mixed with rather more than double its bulk of a similar solution of quinidine marking 24°↗. The resultant solution gave no rotation at all, the one effect perfectly neutralizing the other.

In experimenting upon *non-fluorescent* solutions of quinine or quinidine in the polariscope, it was found that these solutions were still possessed of their original molecular rotation upon plane-polarized light, even undiminished, if care were taken not to dilute the fluid when destroying the fluorescence by the soluble chloride, &c., which was always done by adding it in the solid state.

THE CHEMICAL GAZETTE.

No. CCCLXXXVII.—December 1, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Investigation of Lactic Acid. *By* A. WURTZ.

THE constitution and true equivalent of lactic acid are still matters of doubt. With Gerhardt, most chemists have adopted the formula

$$C^{12}H^{12}O^{12}$$

for this acid, and regard it as bibasic. Nevertheless, the fact of its formation at the expense of the elements of alanine, $C^6H^7NO^4$, seems to indicate that it only contains 6 equivs. of carbon. Strecker, to whom we are indebted for this curious observation, has expressed the opinion that the lactic acid which exists in the liquid of the muscles contains $H^6H^6O^6$, whilst that obtained in the lactic fermentation is represented by the formula $C^{12}H^{12}O^{12}$.

The latter is the acid examined by the author, and he now endeavours to show that it contains only 6 equivs. of carbon, that its constitution is represented by the formula

$$\left.\begin{matrix} C^6H^4O^2 \\ H^2 \end{matrix}\right\} O^4,$$

that it is bibasic, and lastly, that it is one of the simplest of organic acids.

Some time since he showed that lactic acid is one of the products of the slow oxidation of propyloglycol, $C^6H^8O^4$, under the influence of platinum-black. By repeating this experiment, he was enabled to prepare several grammes of lactate of zinc. The crystals obtained were efflorescent, and lost 17·1 per cent. of water in the air. The effloresced salt lost 18·7 per cent. =3 equivs. of water at 212° F. Another sample did not effloresce, lost nothing in the air, and set free 18·1 per cent. of water at 212° F. A portion of this salt required for its solution 52 parts of water at 39° F. Boiling alcohol dissolved it in small quantity; on cooling, a portion of the salt was

deposited in flakes. The dry salt gave the following results on analysis:—

	Found.	Calculated, $C^6H^5ZnO^6$.
Carbon.....	29·4	29·6
Hydrogen....	4·1	4·1

This analysis shows the salt to be lactate of zinc. In its characters it approaches nearer to ordinary lactate of zinc, $C^6H^5ZnO^6$, 3HO, than to that prepared with the acid extracted from the liquid of the muscles. The author cannot, however, settle this question, as he has been unable to procure the salt in any quantity. The operation which furnishes it is very delicate; the oxidation of the propyloglycol by platinum-black often goes too far, when glycolic acid, or even carbonic acid is obtained in place of lactic acid.

This mode of formation of lactic acid is very simple, and exactly comparable to that of acetic acid by the oxidation of alcohol:—

$$\underbrace{C^4H^6O^2}_{\text{Alcohol.}}+O^4=\underbrace{C^4H^4O^4}_{\text{Acetic acid.}}+2HO.$$

$$\underbrace{C^6H^8O^4}_{\text{Propyloglycol.}}+O^4=\underbrace{C^6H^6O^6}_{\text{Lactic acid.}}+2HO.$$

When alcohol is converted into acetic acid, we assume that the oxygen attaches itself to the radical æthyle, C^4H^5, which is modified by substitution to become converted into acetyle, $C^4H^3O^2$. We may suppose that the same thing takes place in the oxidation of propyloglycol, $\left.\begin{matrix}C^6H^6\\H^2\end{matrix}\right\}O^4$. The diatomic radical C^6H^6 becoming modified by substitution, is converted into lactyle, $C^6H^4O^2$. From this it results that the constitution of lactic acid would be expressed by the formula

$$\left.\begin{matrix}C^6H^4O^2\\H^2\end{matrix}\right\}O^4.$$

This formula is justified by the transformations which lactic acid may be made to undergo. When lactate of lime is distilled with twice its weight of perchloride of phosphorus, a colourless liquid passes; this is a mixture of oxychloride of phosphorus and chloride of lactyle, $C^6H^4O^2, Cl^2$. It is difficult to obtain this chloride in a state of purity, as it is partially decomposed by distillation. Nevertheless the following analyses leave no doubt as to its existence and composition:—

	Found.			Calculated.
	I.	II.	III.	
Carbon....	27·6	27·5	29·3	28·3
Hydrogen..	3·3	3·1	3·3	3·1
Chlorine ..	..	..	50·4	55·9

Chloride of lactyle is colourless at the moment of its preparation, but soon blackens when kept, evolving muriatic acid. The analysis III. is that of a liquid in this condition. Its boiling-point is higher

than that of the oxychloride. In contact with water it is decomposed, forming muriatic acid and regenerating lactic acid. A considerable quantity of lactate of lime was prepared from this regenerated lactic acid.

Chloride of lactyle reacts very energetically upon absolute alcohol, forming muriatic acid, hydrochloric æther, and a chlorolactic æther, the analysis of which will be given hereafter Water precipitates it from the alcoholic liquid in the midst of which it is formed. It is easy to prepare it in large quantities by treating with alcohol the mixture of chloride of lactyle and oxychloride of phosphorus obtained in the action of perchloride of phosphorus upon lactate of lime. Water added to the alcoholic liquid dissolves the phosphoric æther formed, and precipitates the chlorolactic æther.

This is a liquid of a very agreeable aromatic odour. Its density at 32° F. is 1·097. It distils without alteration at 302° F. It contains:—

	Found. I.	Found. II.	Calculated.	
Carbon	43·8	44·0	C^{10}	44·2
Hydrogen ..	6·7	6·6	H^9	6·6
Chlorine....	..	25·6	Cl	26·0
Oxygen	..	..	O^4	23·2

These numbers agree with the formula $C^{10}H^9ClO^4$, which was confirmed by the density of vapour of the compound. Experiment gave this density at 4·9; the theoretical density corresponding with the preceding formula for a condensation to 4 vols. is 4·7.

Chlorolactic æther is produced in virtue of the following reaction:—

$$\underbrace{C^6H^4O^2Cl^2}_{\text{Chloride of lactyle.}} + 2C^4H^6O^2 = \underbrace{C^4H^5Cl}_{\text{Hydrochloric æther.}} + H^2O^2 + \underbrace{\left.\begin{matrix}C^6H^4O^2\\C^4H^5\\Cl\end{matrix}\right\}O^2}_{\text{Chlorolactic æther.}}.$$

The acid corresponding with this æther would be chlorolactic acid, a compound of lactic and muriatic acids,—

$$\left.\begin{matrix}C^6H^4O^2\\H^2\end{matrix}\right\}O^4 + HCl = \left.\begin{matrix}C^6H^4O^2\\H\\Cl\end{matrix}\right\}O^2 + H^2O^2.$$

In this acid, as in its æther, chlorine is substituted for the group HO^2.

At any rate, the vapour-density of chlorolactic æther proves that the acid in it, which is derived from chloride of lactyle, contains, like the latter, only 6 equivs. of carbon. The mode of formation of this chloride, its constitution, and the action which it exerts upon water, throw much light on the constitution of lactic acid itself. This acid is bibasic, for it is derived from a diatomic chloride. It contains the diatomic radical lactyle, $C^6H^4O^2$, which exists in this chloride. It contains 2 equivs. of hydrogen outside the radical,

and which are capable of being replaced by 2 equivs of metal*. This becomes evident, if we consider the reaction of chloride of lactyle upon water, which is expressed by the following equation:—

$$\underbrace{C^6 H^4 O^2, Cl^2}_{\text{Chloride of lactyle.}} + \left.\begin{matrix} H^2 \\ H^2 \end{matrix}\right\} O^4 = \underbrace{\left.\begin{matrix} C^6 H^4 O^2 \\ H^2 \end{matrix}\right\} O^4}_{\text{Lactic acid.}} + H^2 Cl^2.$$

Comptes Rendus, June 21, 1858, p. 1228.

On Compounds of Chloride of Aluminium with the Chlorides of Sulphur, Selenium, and Tellurium. By R. WEBER.

If a mixture of chloride of aluminium and pure dichloride of sulphur, $S^2 Cl$, be placed in the bulb of a bulb-tube, and gently heated, a red mass is formed, which constantly becomes lighter when further heated in a current of chlorine gas. Reddish chloride of sulphur distils off, and an oily fluid is formed in the bulb; this, after the excess of chlorine has been driven off by heat, forms white fumes when the temperature is raised, and, on cooling, solidifies into a yellow crystalline mass. This substance is

Double Chloride of Aluminium and Sulphur, $Al^2 Cl^3 + SCl^2$; it is fusible at 212° F., and decomposes with water, with a strong evolution of heat. In this reaction some sulphur separates, and the solution contains alumina, sulphuric acid, and hyposulphuric acid. The compound may be distilled in a closed bent tube. When heated with sulphur, the compound acquires a deep red colour; at the same time it becomes fluid, and chloride of sulphur distils off. This red compound probably contains a chloride of sulphur with more sulphur than the dichloride, $S^2 Cl$. Analysis:—

Cl	80·16	80·53	5	80·34
S	8·88	8·15	1	7·27
Al	11·15	11·32	2	12·39

Double Chloride of Aluminium and Selenium, $Al^2 Cl^3 + SeCl^2$.—The chloride of selenium corresponding with selenious acid, $SeCl^2$, furnishes with chloride of aluminium a similar compound to that formed with chloride of sulphur. It is yellowish white, fuses at 212° F. into an oily fluid, which becomes darker by heating, and dissolves in water without separation of selenium. Analysis:—

Cl	71·38	5	72·59
Se	17·68	1	16·19
Al	10·94	2	16·22

Chloride of tellurium, $TeCl^2$, also combines with chloride of aluminium to form

Double Chloride of Aluminium and Tellurium, $Al^2 Cl^3 + TeCl^2$.—

* Brüning, a few months since, described some lactates containing, according to him, 4 equivs. of metal, the equivalent of lactic acid being represented by $C^{12} H^{12} O^{12}$. This fact supports the opinion above expressed.

This compound is less stable than the preceding, and is decomposed by boiling with water. Analysis:—

Cl	64·16	63·86	5	65·96
Te	25·03	25·91	1	23·87
Al	10·81	9·81	2	10·17

Poggendorff's *Annalen*, civ. p. 421.

On the Conversion of Acetic Acid into Methylic Alcohol. By C. Friedel.

The experiments of Kolbe on the electrolysis of the salts of the fatty acids have shown that the radicals of the acids may be decomposed, giving origin to the radical of the alcohol which contains 2 equivs. of carbon less than the acid.

The formation of the acetones may be regarded as an analogous fact, only that, two molecules of acid being present, the radical of one is decomposed, and the radical C^nH^{n-1}, which is thus produced, forms a double radical with the undecomposed group. This is what has been assumed from the theoretical views of Gerhardt and Chancel, and the experiments of Williamson upon the formation of the mixed acetones. Hitherto, however, the existence of these alcoholic radicals in the acetones has not been proved.

The action of muriatic and hydriodic acids upon acetic acetone has furnished this demonstration, and at the same time an easy means of converting acetic acid into methylic alcohol.

At the ordinary temperature and pressure muriatic acid has scarcely any action on acetone. Still this substance dissolves muriatic acid in considerable quantities; and if the solution be enclosed in a thick matrass hermetically sealed, and heated in the water-bath for eight or ten hours, the liquid separates into two strata. When the matrass is opened, an abundant evolution of gas takes place with an ebullition which carries off a portion of the liquid, unless the vessel be cooled with ice. The gas evolved burns with a green flame, and by analysing it eudiometrically, it was found to furnish a volume of carbonic acid rather larger than its own. Chloride of methyle would furnish exactly its volume of carbonic acid. The excess of carbon found is due to a little acetone, from which the gas is freed with difficulty; it may be removed in part by means of water and distillation.

The remaining liquid also contains a little acetone and an acid possessing the odour of acetic acid, boiling between 212° and 248° F.; with oxide of silver this forms a salt which crystallizes in white needles and contains 64·31 of silver. The acetate contains 64·66. The acid is therefore acetic acid regenerated in a reaction which may be expressed by the following equation:—

$$2(C^6H^6O^2)+4HCl=C^4H^4O^4+4(C^2H^3Cl).$$

To collect the æther produced more readily, the author substituted gaseous hydriodic acid for muriatic acid. Hydriodic acid acts upon acetone at the ordinary temperature, and as soon as the

acetone is saturated with hydriodic vapours, it may be distilled, and furnishes much iodide of methyle and acetic acid.

The iodide of methyle passes in distillation almost entirely between 109° and 113° F., but nevertheless it still contains acetone and cannot easily be obtained pure. By treating it with oxalate of silver in a closed matrass heated in the water-bath, oxalate of methyle is obtained, boiling between 320° and 331° F., and crystallizing in fine laminæ. Its analysis gave—

	Found.	Calculated.
C	40·72	40·67
H	5·34	5·07

This oxalate, treated with potash, furnished wood-spirit, boiling between 149° and 156° F., which, when rectified first over quicklime and then over fused potash, gave the following numbers:—

	Found.	Calculated.
C	37·31	37·50
H	12·59	12·50

In this reaction, besides iodide of methyle, only acetic acid is produced. The portions of the acid boiling at the highest temperatures, furnished, with oxide of silver, only acetate of silver, containing 64·08 per cent. of silver. The action of iodide of phosphorus upon aqueous acetone gives the same results as that of hydriodic acid; but the most convenient method consists in heating acetone with a concentrated aqueous solution of hydriodic acid in a matrass.

As is shown by the formula above indicated, 4 molecules of æther are produced from 2 molecules of acetone. Taking as a starting-point 4 molecules of acetic acid, we may regard the reaction in question as completing a decomposition of the acetyle radicals which they contain, which is commenced by their conversion into acetone.

It is probable that this reaction is general, and that it will allow us to pass from any acid to an inferior alcohol, and consequently from one alcohol to any inferior alcohol. It at the same time furnishes us with a reagent which will allow us to study even the radicals of the acids.—*Comptes Rendus*, June 14, 1858, p. 1165).

Action of Sulphuric Acid upon the Compounds of Barium, Strontium, and Calcium. By MM. LIÈS-BODART *and* JACQUEMIN.

Compounds of Barium.—Monohydrated sulphuric acid dissolves the compounds of barium, as is proved by the authors' experiments upon the oxide, sulphuret, chloride, chlorate, iodate, nitrate, phosphate, borate, chromate, carbonate, oxalate, formiate, acetate, butyrate, valerate, benzoate, cinnamate, and tartrate. Bisulphate of baryta is formed, and the acid of the compound is set free, as shown by the following general equation:—

$$\bar{R}O, BaO + S^2O^6, 2HO = \bar{R}O, HO + S^2O^6, BaO, HO.$$

When these solutions are left standing in a test-glass, a continual formation of radiated needles is observed from day to day; these are grouped in silky tufts, which clothe the walls. This bisulphate could not be accurately analysed, because the authors could not, by means of absorbent tiles, entirely free the crystals from the acid with which they are impregnated, but the authors were led to assume, with Berzelius, the existence of the bisulphate for two reasons.

When these needles are heated upon a plate of platinum, fumes of sulphuric acid are evolved in great abundance, and there remains a deposit of neutral sulphate. And when a given weight of this body is treated with water, neutral sulphate of baryta is precipitated; this is collected on a filter, and its weight is less than that obtained by the precipitation of the filtered liquid by a baryta-salt. The superior weight cannot evidently arise from the uncombined acid alone; it is the result of this excess of acid and of the equivalent of sulphuric acid set free by the decomposition effected by water.

The authors have determined the solubility in sulphuric acid of a certain number of compounds of barium, and obtained the following numbers:—

1	part	of oxide	is soluble	in	35	parts	of acid.
1	„	sulphuret	„	„	35	„	„
1	„	chloride	„	„	30	„	„
1	„	sulphate	„	„	45	„	„
1	„	nitrate	„	„	40	„	„
1	„	phosphate	„	„	30	„	„
1	„	borate	„	„	30	„	„
1	„	chromate	„	„	40	„	„
1	„	carbonate	„	„	35	„	„
1	„	oxalate	„	„	25	„	„
1	„	acetate	„	„	25	„	„

By changing the medium, a rupture of equilibrium is produced in these solutions, and neutral sulphate of baryta is precipitated. This is the effect produced when water is added. Alcohol has the same action, but in certain cases undergoes the action of the acid eliminated. Thus with a solution of nitrate of baryta, nitrous æther is evolved; with chromate of baryta, aldehyde; the acetate and butyrate immediately form the corresponding æthers. Æther behaves in the same way, forming, with the sulphuric acid, the peculiar combination indicated by the authors in a former memoir.

The acetate, butyrate, and valerate, when dissolved in sulphuric acid, present a very interesting peculiarity. It is impossible in this case to perceive the characteristic odour of acetic acid; but as soon as heat is applied, or water added, the acid set free is manifested by its penetrating odour. Butyric and valeric acid also can hardly be detected by the smell.

Strontia and its Salts.—The authors have examined the same salts as for baryta; the results obtained were similar, except the degree of solubility in most cases. The salts of strontia generally dissolve in

sulphuric acid with more difficulty than the corresponding compounds of barium. The numbers obtained for some of them were as follows:—

1	part	of oxide	of strontium	soluble	in	35	of acid.
1	„	sulphuret	„	„	„	40	„
1	„	chloride	„	„	„	40	„
1	„	sulphate	„	„	„	45	„
1	„	nitrate	„	„	„	35	„
1	„	phosphate	„	„	„	40	„
1	„	carbonate	„	„	„	30	„
1	„	oxalate	„	„	„	30	„
1	„	acetate	„	„	„	25	„

Lime and its Salts.—The authors have made the same observations upon lime and its salts. These are less soluble than the compounds of barium and strontium; and even in closed vessels the liquid becomes turbid from day to day, in consequence of a deposit, which 100 parts of sulphuric acid will hardly cause to disappear. The numbers given by the authors are not absolute, as there are variations in the solubility of the same salt according to the mode of operation. Thus on adding successive quantities of sulphuric acid to 1 grm. of phosphate of lime, it required 55 grms. of acid to produce complete solution; but 40 grms. added at once were sufficient. Their results are that—

1	part	of oxide	is	soluble	in	40	parts of acid.
1	„	chloride	„	„	40	„	„
1	„	sulphate	„	„	40	„	„
1	„	nitrate	„	„	30	„	„
1	„	phosphate	„	„	40	„	„
1	„	carbonate	„	„	40	„	„
1	„	oxalate	„	„	30	„	„
1	„	acetate	„	„	25	„	„
1	„	butyrate	„	„	30	„	„
1	„	tartrate	„	„	30	„	„

Comptes Rendus, June 21, 1858, p. 1206.

Note on the Reaction of Perchloride of Phosphorus upon the Essential Oil of Gaultheria procumbens. *By* C. Drion.

In a note presented to the Academy on the 7th of June last, Mr. Couper described some new products which he obtained in the reaction of perchloride of phosphorus upon the oil of *Gaultheria*. He throws some doubts upon the formation of the chloride of salicyle observed by Gerhardt in this reaction, and upon the production of chloride of chlorobenzoyle in the decomposition of that compound under the influence of heat.

The author remarks that, although the chloride of salicyle could not be isolated in a pure state, in consequence of its want of volatility, its existence in the products of the reaction is incontestably established by the facility with which the salicylic æthers are

regenerated in a perfectly pure state by distilling these products with methylic, æthylic, or amylic alcohols.

As regards the chloride of chlorobenzoyle indicated as amongst the products of the decomposition of chloride of salicyle under the influence of heat, its identity has been demonstrated, not only by its conversion into chlorobenzoic acid by contact with water, but also by its conversion, by contact with carbonate of ammonia, into chlorobenzamide, a perfectly crystalline and definite substance.—*Comptes Rendus*, June 21, 1858, p. 1238.

On the Preparation and on some New Compounds of Saccharic Acid. *By* Professor Heintz.

Saccharic acid is best obtained from sugar in the following way:—Two parts of sugar are mixed in a large capsule with 7 parts of crude nitric acid of spec. grav. 1·27, and heated until the commencement of an evolution of gas. The capsule is then removed from the fire. The temperature is raised by the energy of the action of the nitric acid to about 194° F. When it has diminished to 140° F., the capsule is placed over a lamp, and the temperature is kept at 140° F. until the pale yellow fluid becomes brown. The nitric acid is then decomposed almost to the last traces. The mass obtained is diluted with a little water, any oxalic acid separated is removed, the fluid is slightly supersaturated with carbonate of potash, and mixed with acetic acid until it smells strongly of that acid. It is then left standing for several weeks or months. The impure acid saccharate of potash separated is pressed and repeatedly recrystallized with the addition of animal charcoal. A further quantity of the salt crystallizes from the mother-liquor by evaporation. At last, however, a mixture of binoxalate and bisaccharate of potash crystallizes. To obtain the latter from this, the mixture is dissolved in hot water containing acetic acid, and mixed with an excess of acetate of lime until no further precipitate is produced. The filtered fluid then contains no oxalic acid. It is evaporated in the water-bath, and towards the end of the operation supersaturated with ammonia. By this means the saccharate of lime is thrown down. It is separated by filtration, and washed with a little water. By boiling with carbonate of potash, carbonate of lime is formed; this is separated by filtration from the neutral saccharate of potash which remains in solution. On the addition of acetic acid, the filtrate furnishes a crystallization of acid saccharate of potash, which may be purified by recrystallization with the aid of animal charcoal. In this way Heintz has obtained from 3 pounds of sugar 5¼ ounces of acid saccharate of potash, or nearly 11 per cent. of the sugar employed.

Heintz had not been successful in previous attempts to prepare a saccharic æther, because he had supposed that this, like all the then known æthers, would be insoluble, or but sparingly soluble in water. Since then, however, æthers readily soluble in water have been discovered. For this reason Heintz resumed the attempt to prepare the above æther, and soon convinced himself of its existence.

If muriatic acid gas be passed through a solution of saccharic acid in absolute alcohol, and the fluid be neutralized with a carbonate and mixed with æther, there remains, after the evaporation of the filtered solution, a syrupous, bitter substance, which, however, still has an acid reaction, even when the evaporation has taken place at a low temperature, or *in vacuo* over sulphuric acid. The mass, also, does not furnish a perfectly clear solution in water. If it be dissolved in water, the insoluble portion separated by filtration, and the filtrate evaporated under the air-pump, the residue has a stronger acid reaction, and is again not completely soluble in water. It is impossible in this way to obtain a pure saccharic æther. The portion insoluble in water is a very fusible substance. A beautifully crystallizable substance, insoluble in water, may be separated from it; this is volatilizable without decomposition, but Heintz was unable to investigate it more closely, as, notwithstanding his numerous experiments, he only obtained it in very small quantity. In an experiment in which the muriatic acid was neutralized with carbonate of lime and the filtered liquid concentrated by a very gentle heat, small crystals separated, which were found by Heintz to be a compound of saccharic æther with chloride of calcium. This compound is very easily obtained when saccharate of lime is suspended in absolute alcohol and muriatic acid gas is conducted through the mixture. The compound separates in the form of white crystals. To purify it, it is pressed, suspended again in absolute alcohol, and again strongly pressed. It may then be dried over sulphuric acid and lime under the air-pump. It dissolves readily in water, and when this solution is allowed to evaporate over sulphuric acid, the compound crystallizes to the last drop in beautiful crystals, which are stable in the air. It must not however be dissolved in too much water, and especially in hot water, as there is then danger that it may be decomposed. Alcohol, saccharic acid, and chloride of calcium are then produced. This compound is difficult of solution in alcohol, and insoluble in æther. If small crystals of it be placed carefully on water, they dissolve, at the same time moving violently in all directions on the surface of the water. The form of the crystals is a rhombic prism, the angles of which appear to be rather larger than 60°, whilst an oblique terminal surface is set on their acute edge at 95°—100°, the predominance of which causes the crystals to appear tabular. Analysis showed that their composition agrees with the formula $C^{20}H^{18}O^{16} + CaCl$, so that they constitute the chloride of calcium compound of saccharic æther. This compound is exactly analogous to that of lactic æther with chloride of calcium, discovered by Strecker. Both acids are very rich in oxygen. In the expectation that other organic acids rich in oxygen might furnish similar compounds, Heintz has mixed tartaric acid, malic acid, and citric acid with lime and absolute alcohol, and passed muriatic acid gas through them, but without observing any separation of crystals. The æthers of these acids consequently do not combine with chloride of calcium, or at least do not form a compound which is difficult of solution in alcohol.

Heintz has availed himself of the compound of chloride of cal-

cium with saccharic æther, in order to prepare the latter pure. For this purpose it is dissolved in as little water as possible; a little alcohol is added, and it is then mixed with a concentrated solution of sulphate of soda. The mixture is evaporated as rapidly as possible under the air-pump over sulphuric acid, the residue is dissolved in a little absolute alcohol, and a large quantity of æther is added to it. The filtered solution is then again evaporated as quickly as possible under the bell of the air-pump. There remains a perfectly colourless, thick, syrupous fluid, which, when freed as much as possible from all water, alcohol, and æther, sets in a crystalline form. Wherever it covers the surface of the vessel in a thin layer, it often forms very long, concentrically-grouped needles, which present an extraordinary resemblance to Wavellite. Heintz did not succeed in obtaining distinct crystals. The taste of saccharic æther is bitter. When heated, it fuses readily, very soon begins to boil, but then becomes brown and decomposes. It is not volatile without decomposition. The fumes which are evolved when it is heated have a peculiar odour, which is exactly comparable to the taste of walnuts. It dissolves with ease in water and alcohol, and also in æther, but with more difficulty, especially when this is free from alcohol and water. If it be dissolved in the smallest possible quantity of absolute alcohol, and mixed with a similar solution of chloride of calcium, a precipitate of the compound of the latter salt with saccharic æther is produced, especially when the mixture is boiled with the addition of a little alcohol containing muriatic acid.

The attempts to prepare saccharovinic acid have hitherto failed. Once, indeed, Heintz obtained an acid, by agitating acid saccharate of potash with absolute alcohol, exposing it to the action of muriatic acid gas, evaporating the filtered solution over sulphuric acid and caustic lime, extracting the residue with a mixture of absolute alcohol and æther, evaporating the filtered solution, and pouring absolute æther over the residue. In 48 hours crystals were formed, which, when separated from the ætherial solution and dissolved in hot absolute alcohol, crystallized again for the most part on cooling. These crystals were perfectly colourless and transparent. Their form was that of a slender, elongated, unsymmetrical, six-sided prism with angles of about 60°, 140° and 160°. They were terminated by a pair of faces, set straight upon the acute edge; from repeated measurements under the microscope these form an angle of nearly 120°, both with each other and with the acute edge. They dissolve very readily in water and hot alcohol, but with more difficulty in cold alcohol. When the hot, concentrated, alcoholic solution cools in a well-covered vessel, it often remains perfectly unchanged. But if a small crystal of the solid substance be then dropped in, the formation of crystals takes place instantly. This body therefore forms supersaturated solutions with alcohol. The concentrated aqueous solution has a distinct acid reaction. The crystals fuse at 212°—230° F., but appear to be decomposed at this temperature. By treating them with hydrate of

potash and acetic acid, they may be converted into acid saccharate of potash. Their composition, which was ascertained by two perfectly concordant analyses, may be expressed by the empirical formula $C^8 H^5 O^7$. This formula can only be brought to agree with that of saccharic acid by doubling it. It then becomes $C^{12} H^6 O^{12} + C^4 H^5 O + HO$. The body has the same composition as monoæthylocitric acid, which, however, is not yet known in the pure state. Saccharovinic acid should contain two atoms more water, according to the composition of saccharic acid. As notwithstanding numerons experiments Heintz has not succeeded in preparing this substance in tolerable quantity, it must remain undecided whether it is the vinic acid of an acid containing two atoms less water then saccharic acid, or saccharovinic acid itself. In the latter case all the salts of saccharic acid previously investigated by Heintz would necessarily contain two atoms of chemically combined water. The analogy of the composition of the chloride of calcium compounds of lactic and saccharic æther would also be less perfect. The latter must also contain two atoms of water.—*Bericht der Akad. der Wiss. zu Berlin*, 1858, p. 413.

On Iodide of Ethyle. By Dr. De Vrij.

For the preparation of large quantities of iodide of ethyle de Vrij recommends the following method. Absolute alcohol, which must be kept well cooled, is saturated with dry hydrochloric acid gas, and the amount of hydrochloric acid determined in a sample. This alcoholic solution of the gas is then placed in a retort with as much powdered iodide of potassium as is exactly necessary to form chloride of potassium; the mixture is allowed to stand a day, and then the iodide is distilled off, washed, and rectified. In the same manner iodide of methyle may be prepared. On adding wood-spirit saturated with hydrochloric acid to iodide of potassium, an action accompanied with considerable rise of temperature is at once established. Bromide of ethyle is easily prepared by distilling 4 parts of bromide of potassium with 5 parts of a mixture, consisting of 2 parts oil of vitriol and 1 part of alcohol of 96 per cent.—*Journal de Pharmacie*, xxi. p. 169.

ANALYTICAL CHEMISTRY.

On the Testing of Nitric Acid and Nitrate of Soda for Iodine. By Professor Stein.

The problem to be solved is evidently the setting free of the iodine present in the nitric acid in the form of iodic acid (or perhaps more correctly chloride of iodine); in other words, to effect a process of reduction within the strongly oxidizing nitric acid. After several unsuccessful attempts the author employed tin as a reducing agent, and sulphuret of carbon for the detection of the iodine; and this succeeded so perfectly, that iodine could be detected not only

in acid purposely mixed with iodine, but also in commercial nitric acid derived from various sources.

A quantity of the acid to be tested is poured into a test-tube, and a rod of tin is immersed in it until red fumes are distinctly evolved. The rod of tin is then taken out, and a small quantity of sulphuret of carbon is poured in; the mixture is shaken and left quiet for a few moments. The stratum of sulphuret of carbon which usually collects over the acid appears of a red colour, unless the amount of iodine in the acid be too small. With traces of iodine, the colour of this stratum may only be deep yellow. In this case, however, it becomes red, when the sulphuret of carbon is drawn off and evaporated in a small porcelain capsule by blowing upon it.

To show the sensibility of the test, 1 decigramme of iodide of potassium (or 0·076 grm. of iodine) was dissolved in 121 grms. of nitric acid free from iodine; this is nearly 1 : 1600. In this acid the iodine could be very distinctly recognized. This was also the case when it had been diluted to five times the quantity. When diluted to ten volumes, it was no longer possible to detect the iodine by sulphuret of carbon. If the limit of sensibility lies half way between the last two dilutions, it is $\frac{1}{12000}$.

The tin, as may easily be understood, does not act specifically, so that zinc, iron, or copper may be employed in place of it; the action of tin is, however, the most certain. It was also clear that it is not the metal itself that acts in this experiment, but the lower grades of oxidation of nitrogen produced by its contact with the nitric acid. It was proved by direct experiments that it is nitric oxide, the action of which upon iodic acid was already known. This, however, is preferable to sulphuretted hydrogen and all other reducing agents, because it cannot act upon the nitric acid itself, but only quite directly upon the iodic acid. The clearest proof that it is due to the action of nitric oxide is furnished by the red fuming nitric acid of commerce, which need only be diluted with water, to enable iodine to be detected by sulphuret of carbon.

Although one would hardly feel inclined to employ nitric oxide itself instead of tin, the author nevertheless states that the latter has a more certain action than the former. Thus, if iodine be present as chloride of iodine, which, if not always, may certainly sometimes be the case, this is decomposed by tin, but not by nitric oxide.

By means of the test just described, the iodine in nitrate of soda may also be very easily detected. A certain quantity of this salt is put into a test-tube, and water and nitric acid, free from iodine, are poured over it; a rod of tin and sulphuret of carbon are then employed as above described. If sulphuric acid be employed instead of nitric acid to set free the iodine, the result is less distinct in consequence of the simultaneous evolution of chlorine and the formation of chloride of iodine. The sulphuret of carbon is always coloured dark yellow, and the red colour does not make its appearance until a portion of the sulphuret of carbon is volatilized and with it the chlorine.—*Polyt. Centralbl.*, 1858, p. 145.

Further Observations on the Oxidizing Properties of Permanganate of Potash. By M. PÉAN DE SAINT-GILLES.

In the first portion of the author's investigations*, he showed the possibility of converting the hyposulphites, sulphites, and sulphurets into sulphates, completely and rapidly. In indicating the conditions of this transformation, he insisted on the influence of the acid or alkaline nature of the media, having remarked that the oxidation attains its maximum only when these are alkaline. In a memoir on the analysis of gunpowder, MM. Cloëz and Guignet have again brought forward his facts†, and the author now indicates that the results obtained by those chemists, confirm his own in all points.

In his first note the author pointed out a difficulty which frequently opposes the complete peroxidation of the alkaline sulphurets; these sulphurets, when brought in contact with an excess of permanganate, often give rise to a deposition of sulphur, which remains intimately mixed with the precipitate of oxide of manganese, and which cannot be entirely dissolved even by long digestion. The following process allows this difficulty to be easily got over.

The sulphuret is mixed with 1 or 2 grms. of pure potash and boiled. At this moment an excess of an alkaline iodate is added‡; a portion of the sulphur becomes peroxidized by reducing the iodate to the state of iodide, the rest forms a milky deposit which disappears entirely by boiling for a few minutes. In this reaction the sulphur is completely converted into sulphate, as is shown by the two following experiments:—

1. 10 cubic centims. of sulphuret of sodium in solution were treated with an excess of iodate; the liquid was saturated with acid, and precipitated by a salt of barium. The sulphate of baryta weighed 0·097 gr., corresponding to sulphur, 0·0133.

2. Supposing the sulphur to be entirely converted into sulphate, it is evident that the determination of the iodide formed, will furnish exactly the weight of oxygen displaced, and consequently that of the sulphur. In this way 10 cubic centims. of the same sulphuret gave:—

Oxygen absorbed by the sulphuret .. 0·0268 (O^4=400)
Corresponding sulphur ..... 0·0134 (S =200).

The author has also avoided the formation of the deposit of sulphur, by previously precipitating the alkaline sulphuret by an ammoniacal solution of a salt of zinc. The sulphuret of zinc thus produced dissolves entirely in the permanganate.

Pure ammonia in solution does not sensibly reduce the permanganate in the cold, at least for a considerable time§. By continued

* Chem. Gaz., No. 376, p. 236.

† See Chem. Gaz., No. 384, p. 393.

‡ For this purpose the liquid may be employed, which is obtained, according to M. Millon, by dissolving iodine in chlorate of potash with the addition of nitric acid; this liquid must be supersaturated by an alkali.

§ A drop of permanganate dropped into concentrated ammonia, the mixture being exposed to diffused light, was only decolorized in half an hour.

ebullition the reaction is produced, but slowly. Ammonia, however, must be employed with much caution.

The author has already indicated the intimate relations which exist between the reactions of formic acid and those of hydrocyanic acid in contact with the permanganate. He has also observed that, in an alkaline medium, hydrocyanic acid becomes oxidized like formic acid, but that it absorbs an amount of oxygen greater than is necessary to convert all the carbon into carbonic acid, or, what comes to the same thing, all the hydrocyanic acid into cyanic acid. As hydrocyanic acid may be produced by the union of ammonia and formic acid, with elimination of water, the author was led to study the action of the alkaline permanganate upon formiate of ammonia, and found that under these conditions not only is all the formic acid oxidized, but, with it, a great part of the elements of the ammonia. In this case, therefore, a catalytic phænomenon is produced, which reminds one of the solution of platinum in nitric acid by the aid of metallic silver. By oxidizing a small quantity of formiate in presence of a great excess of ammonia, the author was able to displace ten or fifteen times as much oxygen as would have been absorbed by the formiate alone.

The iodides produce an analogous phænomenon.—*Comptes Rendus*, June 14, 1858, p. 1043.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 17, 1858. (The Lord Wrottesley, President, in the Chair.)

"On some new Ethyle-compounds containing the Alkali-metals." By J. A. Wanklyn, Esq.

The very remarkable composition and properties of that class of substances comprehending kakodyle and zinc-ethyle, have justly attached no ordinary degree of interest to the so-called organo-metallic compounds.

Influenced by that interest, I was led to inquire whether the series might not include members into whose composition the alkali-metals entered. It was a question whether combination between so powerfully electro-positive a body as potassium or sodium on the one hand, and a hydrocarbon radical on the other, did not involve impossible conditions. It seemed that the answer to this query would not be valueless as a contribution to the store of facts out of which we may hope some day to evoke the conditions of chemical combination.

My researches in this direction have already enabled me to produce combinations of ethyle with potassium and sodium; and I have little doubt that I shall be able to produce similar compounds containing lithium, barium, strontium, calcium, and magnesium. Combinations containing methyle in place of ethyle will also be sought.

The present paper will be devoted chiefly to the ethyle-compound of sodium.

Sodium-ethyle.

Experiments made with a view to the formation of this body by reactions similar to that by which zinc-ethyle is produced, yielded negative results; but some months ago I made the observation that potassium and sodium decomposed zinc-ethyle, and I found the action to consist in the replacement of a portion of the zinc by the metal employed.

Sodium-ethyle was prepared as follows:—A tube of soft glass was closed at one end and filled with coal-gas. In it was then placed a single clean piece of sodium; its open extremity was then closed with the finger, and whilst still filled with coal-gas, the tube was contracted about the middle, drawn out and bent twice at right angles; pure zinc-ethyle, in quantity about ten times the weight of the sodium, was next introduced, and the tube hermetically sealed. So prepared, the apparatus was afterwards placed in cold water, and left therein for several days, being cautiously shaken up at intervals.

During this time the following changes were noted in the contents of the tube. The sodium became coated with zinc, and gradually disappeared, whilst the total volume of the solid and liquid contents diminished considerably. The liquid became also viscid, and sometimes separated into two portions non-miscible with each other, becoming, however, homogeneous as the operation advanced. There was no evolution of gas.

After the lapse of some days the apparatus was found to contain metallic zinc and a clear colourless liquid. The former was weighed and found to correspond to the sodium dissolved, one equivalent of zinc being precipitated for each equivalent of sodium dissolved.

The clear liquid was made the subject of special examination. It consisted of zinc-ethyle holding in solution a crystalline compound containing sodium, zinc, and ethyle. It was inflammable to the last degree, burning explosively, on exposure to the air, with a yellow flame, and leaving a very alkaline residue. Owing to its extreme tendency to become oxidized, its manipulation presented great difficulties. It was requisite to decant it into bulbs filled with dry hydrogen or coal-gas; and since heat produced partial decomposition, the bulbs had to be double, so that the heated bulb might not receive the liquid.

The clear liquid deposited large quantities of beautiful crystals when cooled to zero; and when gently warmed in a stream of dry hydrogen gas, so long as zinc-ethyle came off it yielded also a mass of crystals. Some crystals were prepared in the latter manner; they fused at about 27° C., but once fused they remained fluid at several degrees below that point. Numerous analytical determinations prove that these crystals contain two equivalents of zinc for every equivalent of sodium, and that their formula is

$$\left.\begin{matrix}\mathrm{Na}\\ \mathrm{C_4H_5}\end{matrix}\right\}, 2\left\{\begin{matrix}\mathrm{Zn}\\ \mathrm{C_4H_5}\end{matrix}\right.$$

The reaction by which they are produced may be thus expressed:

$$6\begin{Bmatrix}\mathrm{Zn}\\ \mathrm{C_4H_5}\end{Bmatrix}+\begin{Bmatrix}\mathrm{Na}\\ \mathrm{Na}\end{Bmatrix}=\begin{Bmatrix}\mathrm{Zn}\\ \mathrm{Zn}\end{Bmatrix}+2\left(\begin{Bmatrix}\mathrm{Na}\\ \mathrm{C_4H_5}\end{Bmatrix},2\left\{\begin{matrix}\mathrm{Zn}\\ \mathrm{C_4H_5}\end{matrix}\right)\right.$$

For the body $\mathrm{Na\,C_4\,H_5\,I}$ I propose the name *sodium-ethyle*, and for the crystals that of *double compound of sodium-ethyle with zinc-ethyle*.

Many attempts were made to obtain sodium-ethyle free from zinc-ethyle, but without success.

By distillation it was found to be equally impossible either to distil off $\begin{Bmatrix}\mathrm{Na}\\ \mathrm{C_4H_5}\end{Bmatrix}$ from the crystals, or to distil off all $\begin{Bmatrix}\mathrm{Zn}\\ \mathrm{C_4H_5}\end{Bmatrix}$ so as to leave pure $\begin{Bmatrix}\mathrm{Na}\\ \mathrm{C_4H_5}\end{Bmatrix}$ behind. When the crystals are moderately heated in a bulb, a singular phenomenon occurs. Gas is evolved, and there remains behind metallic sodium, also metallic zinc, but no carbonaceous residue. This reduction of a sodium-compound by heat alone is an anomaly in chemistry.

When the crystals are heated in the water-bath with potassium, a sudden evolution of gas occurs, and there results metallic zinc, with a liquid alloy of potassium and sodium—a result likewise peculiar.

When the crystals are heated in the water-bath with excess of sodium, evolution of gas likewise takes place.

From these experiments it would seem that the conjoined zinc-ethyle is necessary to the existence of sodium-ethyle; or more precisely, that some adjunct of a less positive nature than sodium-ethyle is requisite to make the existence of the latter possible.

Passing on to the other reactions of the crystals $2(\mathrm{ZnC_4H_5})\}$ $\mathrm{NaC_4H_5}\}$:—

With water there is given pure hydride of ethyle, and hydrated oxides of zinc and sodium. The reaction takes place with great evolution of heat.

With carbonic acid there is given propionate of soda, which unites with zinc-ethyle forming a double compound, decomposed on the addition of water. To the account of this reaction, published elsewhere, I have to add that it takes place without evolution of ethyle or any other gas—a result which further confirms the formula of sodium-ethyle adopted in this paper.

With carbonic oxide there is also a reaction, which is in course of examination.

Cyanogen gas is instantly absorbed, with the formation of a brown solution.

With ether there seems to be no reaction. For the rest, with oxygen, iodine, &c., I should predict reactions quite analogous to those of zinc-ethyle, but have not specially examined the point.

Potassium-ethyle.

Zinc-ethyle and potassium react still more readily than the former body and sodium. So far as at present ascertained, the cases greatly resemble one another. Just as with sodium, I obtain crystals readily

soluble in zinc-ethyle, which contain in this case abundance of potassium.

Seeing that the *kind* of reaction brought under notice in this paper is apparently unique, it is necessary to offer a few observations upon it.

$$2 \cdot \left.\begin{matrix} Zn \\ C_4H_5 \end{matrix}\right\} + \left.\begin{matrix} Na \\ Na \end{matrix}\right\} = 2 \cdot \left.\begin{matrix} Na \\ C_4H_5 \end{matrix}\right\} + \left.\begin{matrix} Zn \\ Zn \end{matrix}\right\}$$

The reaction here formulated may be regarded as an electrolytic decomposition—as an ordinary case of precipitation of one metal by a more electro-positive metal. Here ethyle is the electro-negative, and zinc the electro-positive member: sodium is more electro-positive than zinc, and accordingly sodium displaces zinc.

Following out the hypothesis—where the organo-metallic body contains a metal less electro-positive than the hydrocarbon radical, I should expect that the hydrocarbon radical would be eliminated by the action of sodium. Kakodyle, for instance, should give methyle and arsenide of sodium.

$$\left.\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right\} As + \left.\begin{matrix} Na \\ Na \end{matrix}\right\} = \left.\begin{matrix} Na \\ Na \end{matrix}\right\} As + \left.\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right\}$$

A case in point is afforded by the reaction of the alkali-metals with ammonia.

$$2 \cdot \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N + \left.\begin{matrix} K \\ K \end{matrix}\right\} = 2 \cdot \left.\begin{matrix} K \\ H \\ H \end{matrix}\right\} N + \left.\begin{matrix} H \\ H \end{matrix}\right\}$$

Of the same kind is the reaction of zinc-ethyle upon ammonia*.

$$\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N + \left.\begin{matrix} Zn \\ C_4H_5 \end{matrix}\right\} = \left.\begin{matrix} Zn \\ H \\ H \end{matrix}\right\} N + \left.\begin{matrix} H \\ C_4H_5 \end{matrix}\right\}$$

To develope the hypothesis still further: just as the positive side admits of displacement by a more electro-positive radical, so should the negative side admit of displacement by a more electro-negative body.

The ordinary reactions of zinc-ethyle may be looked upon as illustrating this proposition, and can be written so as to exhibit a double displacement.

$$\overset{+}{Zn},\ \overset{-}{C_4H} + \overset{+}{I}\overset{-}{I} = \overset{+}{Zn}\overset{-}{I} + \overset{+}{C_4H_5}\overset{-}{I}$$

$$\text{also}\quad \overset{+}{Zn}\overset{-}{C_4H_5} + \overset{+}{O}\overset{-}{O} = \overset{+}{Zn}\overset{-}{O} + \overset{+}{C_4H_5}\overset{-}{O}$$

Inspection will show in all these cases, that an electro-positive radical displaces a less electro-positive radical; and an electro-negative radical displaces a less electro-negative one.

* See Frankland's paper, Trans. Royal Soc. 1857.

In accordance with the theory would be the displacement in sodium-ethyle of the ethyle by mercury, or by copper, &c., platinum, &c.

$$\begin{matrix} Na, C_4H_5 \\ Na\ C_4H_5 \end{matrix} + \begin{matrix} Cn \\ Cn \end{matrix} = \begin{matrix} NaCn \\ NaCn \end{matrix} + \begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}$$

Also a like displacement by arsenic or by nitrogen would be according to theory.

Pushing the hypothesis to its furthest limits, I should say that sodium-ethyle is only in *equilibrium* with bodies whose respective electrical sides lie either both of them *within*, or both of them *without* the space lying between the electro-positive sodium and the electro-negative ethyle.

"Note on Sodium-ethyle and Potassium-ethyle." By Edward Frankland, Ph.D., F.R.S.

The recent interesting discovery of sodium-ethyle and potassium-ethyle by Mr. Wanklyn, led me to investigate the cause of the non-formation of these bodies by reactions analogous to those successfully used for the production of zinc-ethyle and similar organo-metallic compounds. In my earlier experiments upon the isolation of the organic radicals, I studied the action of potassium and sodium upon iodide of ethyle, and found that the latter compound was readily decomposed by either of the metals at a temperature of from 100° to 130° C. The separated ethyle was, however, transformed almost completely into hydride of ethyle and olefiant gas, whilst not a trace of potassium-ethyle or sodium-ethyle was produced. Mr. Wanklyn has since repeated this experiment with the addition of ether, and has obtained the same result as regards the non-formation of an organo-metallic compound.

The temperature at which sodium decomposes iodide of ethyle is much lower than that at which sodium-ethyle is broken up, consequently no explanation of the phenomenon can be obtained from this source. In his observations on the formation of ethyle*, Brodie mentions that iodide of ethyle is decomposed at 170° C. by zinc-ethyle; and it therefore occurred to me that sodium-ethyle, owing to its more powerful affinities, might effect the decomposition of iodide of ethyle at a lower temperature than that at which iodide of ethyle is decomposed by sodium; in which case the production of sodium-ethyle, by the action of sodium upon iodide of ethyle, would be an impossibility. Experiment completely confirmed this anticipation. A quantity of a strong solution of sodium-ethyle in zinc-ethyle was thrown up into a dry receiver filled with mercury, and an equal volume of pure iodide of ethyle added to it. Immediately on the mixture of the two liquids, a lively effervescence set in, a considerable quantity of gas collected in the receiver, and a white deposit of iodide of sodium rendered the liquid thick and turbid. The reaction was complete in two or three minutes without the application of heat. An analysis of the gas, previously freed from the vapours of iodide of ethyle and zinc-ethyle, showed it to consist of equal volumes of hydride of ethyle and olefiant

* Journal of the Chemical Society, vol. iii. p. 405.

gas, mixed only with a mere trace of ethyle. This reaction may therefore be thus expressed:—

$$C_4H_5Na + C_4H_5I = NaI + \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\} + C_4H_4.$$

It is therefore evident that sodium-ethyle, and the remark no doubt applies also to potassium-ethyle, could not be obtained by the action of sodium upon iodide of ethyle, even if the decomposition of the latter could be effected at ordinary temperatures, since each particle of the organo-metallic compound being in contact with iodide of ethyle at the moment of its formation, would be instantly decomposed in the manner just described. That olefiant gas and hydride of ethyle, with mere traces only of ethyle, constitute the gaseous product of the decomposition of iodide of ethyle by sodium, is strong evidence that this formation and immediate decomposition of sodium-ethyle actually takes place. Sodium-ethyle thus stands in the same relation to iodide of ethyle as hydride of zinc does to hydriodic acid; and consequently all attempts to produce hydride of zinc by the action of the metal upon the hydrogen acids have failed. These considerations, taken in connexion with Mr. Wanklyn's mode of forming sodium-ethyle and potassium-ethyle, afford a clue to the nature of the reactions by which we shall probably eventually succeed in forming the hydrogen compounds of the highly positive metals. Although the hydrogen compounds of arsenic, antimony, phosphorus, and tellurium are by no means exact analogues of zinc-ethyle, it would nevertheless be interesting to ascertain the action of sodium upon these bodies, with a view to the formation of hydride of sodium.

The nature of the gas evolved by the action of sodium-ethyle upon iodide of ethyle, has some interest in connexion with the formation of ethyle by the action of zinc upon iodide of ethyle. Brodie expressed, in the memoir above alluded to, an ingenious and highly probable hypothesis, that the true source of the ethyle is the decomposition of its iodide by zinc-ethyle, thus:—

$$C_4H_5Zn + C_4H_5I = ZnI + \left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\};$$

and that the secondary products of the reaction (olefiant gas and hydride of ethyle) which always accompany the ethyle, result from the primary action of zinc upon iodide of ethyle, thus:—

$$2(C_4H_5I) + 2Zn = C_4H_4 + \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\} + 2ZnI.$$

The composition of the gases produced in the above reaction of sodium-ethyle upon iodide of ethyle seems, however, to indicate that the reverse of this hypothesis is true, and that the source of the ethyle is to be found in the primary action of zinc upon iodide of ethyle,—

$$2(C_4H_5I) + 2Zn = \left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\} + 2ZnI,$$

whilst the secondary products are derived from the decomposition of iodide of ethyle by zinc-ethyle,—

$$C_4H_5I + Zn\,C_4H_5 = \left.\begin{matrix} C_4H_5 \\ H \end{matrix}\right\} + C_4H_4 + ZnI.$$

THE CHEMICAL GAZETTE.

No. CCCLXXXVIII.—December 15, 1858.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Conversion of Aldehyde into Acetal.
By MM. WURTZ *and* FRAPOLLI.

AT the close of the year 1857, M. Wurtz announced the discovery of an organic chloride derived from aldehyde, and obtained by the action of perchloride of phosphorus upon that body. Its mode of preparation, its boiling-point (136°·4 F.), and its composition, which is represented by the formula $C^4 H^4 Cl^2$, were indicated by him. It is isomeric with the oil of the Dutch chemists. The authors call it *chloride of æthylidene*. It is formed in accordance with the following equation:—

$$\underbrace{C^4 H^4 O^2}_{\text{Aldehyde.}} + \underbrace{PCl^5}_{\text{Perchloride of phosphorus.}} = \underbrace{C^4 H^4 Cl^2}_{\text{Chloride of æthylidene.}} + \underbrace{PO^2 Cl^3}_{\text{Oxychloride of phosphorus.}}$$

This body has since been obtained and described by Geuther*. It appeared to the authors that it might serve to effect the conversion of aldehyde into acetal, and the experiment was the more interesting as one of them had lately proved that glycol treated with sodium and iodide of æthyle does not furnish acetal, but an isomer of that body, diæthyloglycol.

It might have been expected that by treating chloride of æthylidene with æthylate of soda, acetal would be formed, in accordance with the following reaction:—

$$C^4 H^4 Cl^2 + 2\underbrace{\left\{\begin{matrix} C^4 H^5 \\ Na \end{matrix}\right\} O^2}_{\text{Æthylate of soda.}} = 2NaCl + \underbrace{\left\{\begin{matrix} C^4 H^2 \\ (C^4 H^5)^2 \end{matrix}\right\} O^4}_{\text{Acetal.}},$$

This was not the case; the principal product of the action is not acetal, but a chlorinated gas containing $C^4 H^3 Cl$, identical in its composition and properties with the chloride of aldehydene or chlo-

* Chem. Gaz. vol. xvi. p. 267.

rinated æthylene derived from the Dutch oil. This identity was established by two methods,—1st, by determining the solubility of the two gases in water and alcohol; 2ndly, by treating the gas derived from aldehyde with chlorine. According to the authors' experiments:—

1 vol. of water at 77° F. dissolves 0·81 vol. of chlorinated æthylene, $C^4 H^3 Cl$, produced from the oil of the Dutch chemists.

1 vol. of water at 77° F. dissolves 0·81 vol. of chloride of aldehydene, $C^4 H^3 Cl$, produced from aldehyde.

1 vol. of absolute alcohol at 73°·2 F. absorbs 54·5 vols. of chlorinated æthylene.

1 vol. of absolute alcohol at 72°·5 F. absorbs 55·1 vols. of chloride of aldehydene.

Chloride of aldehydene derived from aldehyde absorbs chlorine, and forms a compound, $C^4 H^3 Cl^3$, identical with that obtained by M. Regnault, by treating with chlorine the gas obtained from the Dutch oil. The identity of these two gases is a curious fact; it marks the intimate relation, and as it were the meeting-point of two series of isomeric compounds, the one derived from glycol, the other from aldehyde.

One of the authors has recently shown that glycol on becoming dehydrated furnishes aldehyde; but aldehyde does not reproduce the compounds of glycol. Thus chloride of æthylidene differs from its isomer, the Dutch oil; the interesting compound which M. Geuther* has just obtained by combining aldehyde with anhydrous acetic acid differs from diacetic glycol, and acetal differs from diæthyloglycol. But these two series, although distinct, present an intimate connexion, and the authors prove the possibility of passing from one to the other. It is the chloride of aldehydene that furnishes the means.

From the differences existing in the affinities of chlorine, bromine, and iodine, reactions often succeed with bromides and iodides, which fail with chlorides. Organic chemistry presents many examples of this peculiarity, and the following is a new one. Bromide of æthylidene furnishes acetal when it is treated with æthylate of soda. The reaction is represented by the equation formulated above; it takes place with remarkable energy. The difficulty of this experiment consists in the formation of the bromide of æthylidene. This body is produced when vapours of aldehyde are passed into refrigerated pentabromide of phosphorus. Oxybromide of phosphorus and bromide of æthylidene are formed. These two bodies cannot be separated by fractional distillation, as the organic bromide would be decomposed. It is freed from the oxybromide by agitating the mixture with fragments of ice, which are replaced in proportion as they melt. This operation furnishes a dense yellow liquid, insoluble in water, and becoming rapidly decomposed by contact with that fluid when the temperature rises a little; it continually emits vapours of hydrobromic acid, and it is impossible, in consequence of the ease with which it is altered, not

* Chem. Gaz. vol. xvi. p. 305.

only to prepare it in a state of purity, but even to preserve it without decomposition. This liquid is bromide of æthylidene.

The following is the analysis of the acetal formed by the reaction of this body with æthylate of soda:—

	Found.		Calculated.	
Carbon	61·2	..	C^{12}	61·02
Hydrogen	..	12·08	H^{14}	11·86
			O^4	27·12

The conversion of aldehyde into acetal by the agency of bromide of æthylidene is a very laborious operation. It succeeds easily by the following process, which allows it to be effected in two perfectly distinct phases, so as to follow this curious transformation step by step.

Aldehyde is mixed with twice its volume of absolute alcohol; the liquid is placed in a freezing mixture, and a current of muriatic gas is passed into it until complete saturation. There are then two strata in the vessel; an upper ætherial one, which is collected; and an inferior aqueous one, saturated with muriatic acid, which is thrown away. The ætherial liquid contains chlorine. It represents a compound intermediate between acetal and chloride of æthylidene. Its composition is represented by the formula

$$C^8 H^9 ClO^2 = \left\{ \begin{matrix} C^4 H^4 \\ C^4 H^5 \\ Cl \end{matrix} \right\} O^2,$$

in which chlorine takes the place of the group $C^4 H^5$, O^2 of acetal, $\left\{ \begin{matrix} C^4 H^5 \\ C^4 H^5 \\ C^4 H^5 \end{matrix} \right\} \begin{matrix} O^2 \\ O^2 \end{matrix}$.—It is formed in accordance with the following equation:—

$$C^4 H^4 O^2 + C^4 H^6 O^2 + HCl = C^8 H^9 ClO^2 + H^2 O^2.$$

The following is its analysis:—

	Experiment.			
	Product boiling at 203°—206°·6 F.	Product boiling at about 208° F.	Theory.	
Carbon	45·14	..	C^8	44·24
Hydrogen..	9·51	..	H^9	8·29
Chlorine ..	..	30·34	Cl	32·72
Oxygen....	..	..	O^2	14·75

As the body is partially decomposed by distillation, the analysis could hardly be expected to be more exact.

In reacting upon æthylate of soda, the compound $C^8 H^9 ClO^2$ furnishes chloride of sodium and acetal:—

$$C^8 H^9 ClO^2 + \underbrace{\left\{ \begin{matrix} C^4 H^5 \\ Na \end{matrix} \right\} O^2}_{\text{Æthylate of soda.}} = ClNa + \underbrace{C^{12} H^{14} O^4}_{\text{Acetal.}}$$

The alcohol obtained possesses all the properties attributed by

M. Stas to this body. It boils at 219°·2 F. It gave the following results on analysis:—

	Experiment.		Theory.	
Carbon.....	61·36	60·80	C^{12}	61·08
Hydrogen....	12·40	12·36	H^{14}	11·86
			O^4	27·06

Acetal and diæthyloglycol are isomeric. The difference in their constitution probably resides in some difference of structure in the radicals $C^4 H^4$, of which one, æthylene, enters into the composition of diæthyloglycol, whilst the other, æthylidene, is the base of aldehyde and acetal.—*Comptes Rendus*, September 6, 1858, p. 418.

On Trehalose, a new kind of Sugar. By M. Berthelot.

For some years past the study of the sugars has been gaining fresh importance; the relations which exist between these matters and the other organic compounds have been multiplied, and their chemical function has been assimilated to that of the polyatomic alcohols. At the same time a more attentive study of the proximate principles contained in living organisms, has led to the discovery of various new saccharine substances, endowed with remarkable properties, such as dulcine, quercite, pinite, sorbine, inosite, melitose, mycose, &c. The author has had occasion to study the crystallizable saccharine principles derived from various vegetables; amongst these some are new, and others identical with substances already known, but extracted from new sources.

I. *Trehalose.*—A manna sent from Turkey to the French Universal Exhibition under the name of *trehala**, furnishes a new sugar analogous to cane-sugar; to this the author gives the name of *trehalose.*

To obtain the sugar, the pulverized manna is treated with boiling alcohol; sometimes the trehalose crystallizes immediately, sometimes it is necessary to concentrate it to the consistence of a syrup and to leave it standing for some days. The crystals are isolated, pressed, washed with cold alcohol, boiled with a small quantity of alcohol to purify them, and then dissolved in boiling alcohol, in the presence of animal charcoal. The cold liquid deposits the crystals, which are recrystallized from alcohol two or three times. These crystals are trehalose. They are right rhomboidal prisms, of which the appearance and angles are quite distinct from those of cane-sugar and the other known saccharine matters.

From analysis, trehalose dried at 284° F. may be represented by the formula $C^{12} H^{11} O^{11}$. At ordinary temperatures it retains a

* The *trehala*, according to M. Guibourt (*Comptes Rendus*, June 21, 1858, p. 1213), consists of the cases in which a beetle of the Curculionidous (or Weevil) tribe undergoes its transformations. The cases are composed principally of amylaceous matter, collected from the pith of a species of *Echinops*, on which the insect lives.

certain quantity of water of crystallization. The crystals crunch under the teeth and possess a strongly saccharine taste.

Trehalose is very soluble in water, but nearly insoluble in cold alcohol, although it dissolves readily in boiling alcohol. Its rotatory power, in relation to the tint of passage, is equal to +208°; this number was deduced from observations made upon an aqueous solution containing 13 per cent. of trehalose. The amount of deviation does not alter in the space of twenty-four hours. This power is nearly three times that of cane-sugar, and greater than that of any known sugar, including mycose.

Trehalose, when heated, melts at about 248° F., forming a colourless liquid, and solidifies on cooling into a mass resembling barley-sugar. It may be kept at 356° F. without undergoing any perceptible alteration, a condition in which cane-sugar and the other fermentescible sugars at present known are completely destroyed. When heated above 392° F., trehalose loses water, and becomes converted into an insoluble black matter, with evolution of gas and an odour of caramel. In the open air it burns with a reddish flame, and leaves a coal which burns without residue. Under the influence of yeast, trehalose only ferments very slowly and imperfectly.

Potash and baryta do not alter it at 212° F.; ammoniacal acetate of lead precipitates it. It does not distinctly reduce potassiotartrate of copper. When heated to 212° F. with fuming muriatic acid, it becomes blackened and slowly destroyed; with concentrated sulphuric acid it is rapidly carbonized at 212° F. Nitric acid converts it into oxalic acid, without any mucic acid being formed.

Trehalose heated to 356° F. with stearic acid, benzoic acid, &c., forms a small quantity of neutral compounds analogous to the fatty bodies.

1 part of trehalose was dissolved in about 9 parts of water, and ½ part of concentrated sulphuric acid was added; the mixture was then heated to 212° F. The deviation of the plane of polarization by the original liquid was equal to +37°·5. In a quarter of an hour it was +37°, and the liquid scarcely reduced potassiotartrate of copper. In an hour the deviation was equal to +36°·5, and the reduction was weak; in five hours the deviation was +11°, and the reduction enormous. Two hours' further exposure to 212° F. produced no other change except a strong coloration of the liquid; the rotatory power did not sensibly vary. The acid was saturated with carbonate of lime, the liquid was evaporated, and the residue treated with alcohol, &c.; this furnished an uncrystallizable saccharine syrup analogous to liquid sugar. This *trehalic glucose* reduces potassiotartrate of copper and is destroyed by alkalies at 212° F.; with yeast it ferments readily and completely, forming alcohol and carbonic acid. The slowness with which trehalose is modified under the influence of sulphuric acid is well worthy of attention.

From the preceding characters, trehalose constitutes a new sugar, analogous to cane-sugar, but far more stable. By its resistance to the action of heat, of acids, and of yeast, it behaves like a substance

intermediate between the group of sugars properly so-called, and the principles which contain an excess of hydrogen, such as mannite, dulcine, and glycerine.

II. *Javanese Palm-sugar* (from *Saguerus Rumphii*).—Of this sugar the author has obtained fine crystals, exactly identical with those of cane-sugar by the numerical value of their angles and of their rotatory power. Their reactions were exactly the same. This sugar is manufactured in Java on a large scale.

III. *Sugar of Sorgho.*—Crystals identical with those of cane-sugar.

IV. *Maple-sugar.*—This sugar is generally assimilated to cane-sugar. The angles of its crystals and its rotatory power are identical with those of cane-sugar.

V. The fruits of the *Carob-tree* furnish a crystallizable sugar, of which the rotatory power and the reactions are identical with those of cane-sugar.

VI. The author has also investigated the saccharine matters of the Asphodel, of the *Hedysarum alhagi*, and of the Briançon manna; he promises the results at a future day.—*Comptes Rendus*, June 28, 1858, p. 1276.

On the Compounds of the Æthylic and Methylic Hydrosulphuric Æthers with Biniodide of Mercury. *By* A. Loir.

In a former memoir* the author investigated the compounds which the hydrosulphuric æthers furnish by combining with certain metallic chlorides; in the present he describes the compounds formed by the same æthers with biniodide of mercury.

Æthylic hydrosulphuric æther, when brought in contact with solution of bichloride of mercury, combines with and gives origin to the compound $C^4 H^5 S, HgCl$. The combination of this æther with biniodide of mercury does not take place directly; it is, however, effected by two processes, in which these two bodies, being formed by double decomposition, combine in the nascent state.

The first process consists in heating for some hours to 212° F. in a sealed tube, a mixture of alcohol, hydriodic æthylic æther, and the compound $C^4 H^5 S, HgCl$. The hydriodic æther reacts upon the bichloride, forming hydrochloric æther and biniodide of mercury, as indicated by M. Schlagdenhauffen. This iodide then combines with the hydrosulphuric æther. The tube contains two strata of fluid. The lower one, which is yellow, quickly solidifies; the upper one, on cooling, deposits a yellow crystalline body.

In the second process, bisulphuret of mercury, in fine powder, is heated to 212° F. in a sealed tube with a mixture of hydriodic æther and alcohol; a yellow crystalline body is deposited on cooling, which is separated from the sulphuret not acted upon. This method, applied to other sulphurets, furnishes crystalline compounds.

The yellow compound thus obtained, purified by boiling alcohol, in which it is but sparingly soluble, and dried over sulphuric acid,

* Chem. Gaz. vol. xi. p. 361.

presents the appearance of sulphur; when rubbed against a hard body, it does not change colour. This compound fuses at 230° F.; on cooling it crystallizes in needles radiating round different centres. At a temperature above 356° F. it is decomposed, setting free hydrosulphuric æther; yellow iodide of mercury, passing to red, is volatilized. Its analysis leads to the formula $C^4 H^5 S, HgI$.

	Found.	Calculated.
Carbon	8·25	8·8
Sulphur.....	6·40	5·9
Hydrogen.....	2·50	1·8
Mercury	35·75	36·7
Iodine	47·90	46·8

The compound of methylic hydrosulphuric æther with biniodide of mercury is obtained by both the above processes, by substituting methylic for æthylic compounds. The yellow product, purified by boiling alcohol, fuses at 188°·6 F., and is decomposed at a temperature above 329° F., furnishing methylic hydrosulphuric æther and biniodide of mercury. Analysis:—

	Found.	Calculated ($C^2 H^3 S, HgI$).
Carbon	4·1	4·6
Mercury.....	37·3	38·7

Comptes Rendus, June 28, 1858, p. 1280.

Investigation of the Alkaloids of Nux Vomica.
By P. Schutzenberger.

Some years since M. Desnoix pointed out a new base, igasurine, in *Nux vomica*, differing from brucine by its greater solubility in water, but he has published no analysis to establish its composition and equivalent. The author having received several samples of igasurine as brucine, has endeavoured to supply this desideratum, but after three analyses, he found, from the difference of his results, that his product was not homogeneous.

By treating his samples with hot water, he succeeded in separating nine new alkaloids, differing in composition, the separation of which may be effected by making use of their different solubility in hot water, and the time which they take to crystallize during the cooling of the liquid. Probably, had the investigation been continued, a greater number of distinct bodies would have been discovered. To establish the existence of each of these bases with certainty, they were all analysed twice, and the second analysis was made with a recrystallized product. The agreement of the two results proved the homogeneity of the substance.

These bases are all colourless, and of a very bitter and persistent taste. Their action upon the animal œconomy is nearly as energetic as that of strychnine. They are all soluble in boiling water, although in very different degrees. They crystallize in transparent needles, or in nacreous tufts, sometimes of considerable size. Nitric acid colours them red like brucine. They all contain water

*

of crystallization (6 or 8 equivs.), which is eliminated at 212° F. None of them melt in their water, although some soften. Two of them may affect the resinous state, but this condition is not stable.

The following is a Table of these bases which the author names *igasurines, a, b, c, d, e, f, g, h, i*:—

	Strychnine	$C^{42}H^{22}N^{2}O^{4}$.
	Brucine	$C^{46}H^{26}N^{2}O^{8}+8$ Aq.
a.	$C^{44}H^{26}N^{2}O^{6}+6$ Aq,	very sparingly soluble.
b.	$C^{36}H^{24}N^{2}O^{14}+6$ Aq,	sparingly soluble.
c.	$C^{36}H^{24}N^{2}O^{8}+6$ Aq,	tolerably soluble.
d.	$C^{34}H^{32}N^{2}O^{16}+6$ Aq,	tolerably soluble.
e.	$C^{36}H^{26}N^{2}O^{8}+6$ Aq,	
f.	$C^{42}H^{30}N^{2}O^{8}+6$ or 8 Aq,	tolerably soluble.
g.	$C^{42}H^{28}N^{2}O^{12}+6$ Aq,	very sparingly soluble.
h.	$C^{42}H^{26}N^{2}O^{12}+6$ Aq,	tolerably soluble.
i.	$C^{40}H^{26}N^{2}O^{14}+6$ Aq,	tolerably soluble.

These bases resemble brucine in their chemical characters, except their greater solubility in water and alcohol. They may be regarded as products of the gradual transformation of brucine under the oxidizing influence of the vital forces.—*Comptes Rendus*, June 21, 1858, p. 1234.

On the Preparation of the Monosulphuret of Potassium.
By Dr. Alex. Bauer.

The author has instituted a long series of experiments upon the preparation of monosulphuret of potassium, from which it appears that:—

1. Monosulphuret of potassium can never be obtained pure by the reduction of sulphate of potash by means of charcoal.

Besides monosulphuret of potassium there is always a formation of a higher sulphuret and free alkali, the sulphuric acid of the sulphate of potash being always reduced before the potash, by which means a mixture of a higher sulphuret and oxide of potassium is formed; and because

2. In the further heating of this higher sulphuret of potassium with charcoal and alkali, no more monosulphuret of potassium is formed, even when the alkali is present in great excess.

3. Hydrogen employed as a reducing agent of sulphate of potash behaves in this respect exactly like charcoal.

4. By the action of gaseous sulphuretted hydrogen upon perfectly dry carbonate of potash at a temperature rising to 320° F., only a very little hydrosulphate of sulphuret of potassium is formed.

5. The action of sulphuretted hydrogen gas upon a solution of carbonate of potash does not expel the carbonic acid, but bicarbonate of potash and an equivalent quantity of hydrosulphate of sulphuret of potassium are formed.

6. A solution prepared by passing sulphuretted hydrogen into solution of potash, and subsequently adding an equal quantity of potash, may be completely decomposed by carbonic acid.

This is also the reason why a solution of carbonate of potash, saturated with sulphuretted hydrogen, continually smells of sulphuretted hydrogen. The sulphuret is again decomposed by the second equivalent of carbonic acid.

7. All the facts ascertained are opposed to the supposition that a solution prepared by mixing a solution of potash saturated with sulphuretted hydrogen gas, with an equal quantity of potash, contains monosulphuret of potassium, or that sulphuret of potassium can be dissolved in water without decomposition.

If, therefore, there be a monosulphuret of potassium, it can only exist in the solid state, and must be prepared directly. This also must be attended with great difficulty.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xxx. p. 285.

On Sulphuret and Perfluoride of Niobium. *By* H. Rose.

Sulphuret of niobium may be obtained from niobic acid and perchloride of niobium in the same way as sulphuret of tantalum from tantalic acid and the perchloride of tantalum. As, however, niobic acid may in general be reduced with far more ease than tantalic acid, niobium may be more easily combined with sulphur, and at a lower temperature, than tantalum.

If niobic acid be treated with vapour of sulphuret of carbon, the production of sulphuret of niobium takes place even at a red heat, so that it may be effected in apparatus formed of hard glass. The author, however, preferred exposing niobic acid to the vapour of sulphuret of carbon when heated to a white heat in a porcelain tray enclosed in a tube of the same material.

In several experiments sulphuret of carbon was conducted over the niobic acid by means of a stream of hydrogen gas. In this way the experiments were rather less accurate, because at the high temperature an imponderable trace of carbon separated from the sulphuret of carbon. It was therefore found to be far more advisable to conduct the sulphuret of carbon over the niobic acid by a current of carbonic acid gas.

The sulphuret of niobium thus obtained is a black powder, which certainly acquires a metallic lustre when rubbed in an agate mortar, but still remains perfectly black, and is thus essentially distinguished from sulphuret of tantalum. It is a conductor of electricity.

Like the analogous sulphuret of tantalum, sulphuret of niobium is not analogous in its composition with niobic acid, but it has essentially the composition $Nb^2 S^3$, although with rather less sulphur.

If sulphuret of niobium be converted into niobic acid by ignition in contact with the atmosphere, the same quantity of acid is obtained as was employed in the preparation of the sulphuret. It will be seen hereafter that this result is of importance.

If sulphuretted hydrogen gas be passed over perchloride of niobium, sulphuret of niobium may be produced, with formation of hydrochloric acid gas, at a far lower temperature. Perchloride of

niobium is blackened by sulphuretted hydrogen even at ordinary temperatures, but for complete decomposition the aid of heat is necessary. In this way a sulphuret of niobium is obtained containing a little more sulphur, and the composition of which agrees better with $Nb^2 S^3$, as in its preparation a far lower heat has been employed than in the production of sulphuret of niobium by means of sulphuret of carbon.

Sulphuret of niobium is not acted upon by chlorine gas at ordinary temperatures, by which it is essentially distinguished from the sulphuret of tantalum prepared from the chloride. But when gently heated it is converted into a dark yellow woolly mass, which consists of a compound of perchloride of niobium and chloride of sulphur; and this, when more strongly heated, melts into a dark yellow fluid, and then sublimes. If the sulphuret of niobium has been carefully prepared, it leaves no residue after being heated when treated with chlorine gas.

While tantalic acid cannot be converted into sulphuret of tantalum by means of sulphuretted hydrogen gas at a high temperature, sulphuret of niobium may be obtained by its means from niobic acid at a strong red heat. It is difficult, however, to prepare it in a state of great purity.

If niobate of soda be treated at a red heat with sulphuretted hydrogen gas, no sulphosalt is formed, as the sulphuret of niobium is not a persulphuret. Sulphuret of niobium is produced, together with hydrosulphuret of sulphuret of sodium, which may be separated from the former by solution in water. The sulphuret of niobium, however, is not pure, but still contains acid niobate of soda, which has been rendered insoluble in water by ignition.

Hydrated niobic acid dissolves readily in aqueous hydrofluoric acid, and this solution furnishes, with other metallic fluorides and with hydrofluoric acid, a series of crystallized double salts, some of which only have been prepared.

Fluoride of Niobium and Potassium.—If the solution of niobic acid in an excess of hydrofluoric acid be mixed with carbonate of potash, a voluminous precipitate is first of all produced, but this disappears when the solution approaches neutralization. On cooling the hot solution, the salt $KF + NbF^2$ separates. Its solution strongly reddens litmus-paper. It fuses readily in a platinum spoon at a low temperature: a stronger heat renders it infusible and perfectly blue. The residue renders reddened litmus-paper blue.

The solution separated from the salt, gave, on evaporation, another salt, which contains more fluoride of potassium, and has a composition which may be expressed by $4KF + 3NbF^2$. The author leaves it undecided whether this is a peculiar compound or a mixture of the former with fluoride of potassium.

By the further evaporation of the mother-liquor of this salt it furnishes a considerable quantity of a deliquescent, fibrously-crystalline salt, consisting of pure fluoride of potassium.

If the solution of niobic acid in hydrofluoric acid be mixed with hydrate of potash so that it may still remain acid, and then eva-

porated until the formation of a crystalline film, it furnishes the compound

$$(KF+NbF^2)+(KF+HF).$$

Fluoride of Niobium and Sodium.—When the solution of niobic acid in hydrofluoric acid was mixed with so much carbonate of soda that it still had a weak, but distinct acid reaction, there was produced a crystalline precipitate of the composition

$$(2NaF+NbF^2)+(NaF+HF).$$

When this salt is heated in the platinum spoon, it becomes blue, but does not fuse; when more strongly heated, it again becomes white.

The fluid separated from this salt gave, on further evaporation, a second crystalline salt of the composition

$$(NaF+NbF^3)+(NaF+HF).$$

The mother-liquor from this salt, when preserved for a long time in a platinum dish, deposited a salt in laminar crystals of the composition $NaF+NbF^2$.

From these experiments it is evident that fluoride of niobium can combine in several proportions with the alkaline fluorides and with hydrofluoric acid, and it will probably also be capable of combining in the same way with other metallic fluorides in numerous, but simple proportions.

It is remarkable, however, that amongst the compounds prepared there is not one which corresponds with the neutral niobates. Such a compound must have the composition

$$RF+2NbF^2.$$

The solutions of the compounds of fluoride of niobium with the alkaline fluorides are distinguished by the circumstance that sulphuric acid produces no turbidity in them, and does not precipitate niobic acid from them. To convert fluoride of niobium into niobic acid, the solution must be evaporated with an excess of sulphuric acid.—*Bericht der Akad. der Wiss. zu Berlin*, 1858, p. 445.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Industrial Applications of Baryta. *By* F. Kuhlmann.

Second Part*.

Manufacture of various acids.

In his previous memoir the author indicated the uses to which he has put the chloride of barium which constitutes the base of his operations. He stated particularly that by mixing a concentrated hot solution of chloride of barium with a solution of caustic soda,

* See Chem. Gaz., 1858, p. 406.

hydrated baryta was obtained, and that anhydrous baryta might be economically procured by the calcination of nitrate of baryta prepared from the chloride. The nitrate decomposed by sulphuric acid served for the manufacture of nitric acid without distillation and of artificial sulphate of baryta, and chloride of barium treated in the same way furnishes this sulphate and muriatic acid.

The nitric acid furnished by the new process marks 10° B., and may be employed directly in the preparation of certain nitrates; the muriatic acid, although its density does not exceed 6° B., may find numerous applications, besides its employment in the production of certain chlorides; it may be used in the acidification of bones, in washing animal charcoal, in the composition of acid bleaching baths, &c.

With the view of ascertaining the limits within which the concentration of these acids should be restrained in order to avoid loss by vaporization, the author made a series of experiments, from which it appears—1st, that the dilute nitric acid cannot be directly concentrated beyond 20° or 25° B.; and 2ndly, that the direct concentration of the muriatic acid cannot exceed 14° B., and that it is better to stop below this limit. The maximum fixity of hydrochloric gas in solution is at a density of 14° B.; its boiling-point is then 228° F.

Manufacture of tartaric acid.

Tartaric acid is prepared from bitartrate of potash by saturating the excess of acid of that salt with native carbonate of baryta, and decomposing the neutral tartrate by means of chloride of barium. The ebullition of a solution of bitartrate of potash with native carbonate of baryta produces a liquid which is perfectly neutral, and may even be slightly alkaline.

The tartrate of baryta thus obtained is well washed with cold water, heated, and decomposed with dilute sulphuric acid, in sufficient quantity to remove the whole of the baryta of the tartrate. The solution furnishes tartaric acid, the whole of which crystallizes readily; the deposit of very heavy sulphate of baryta is washed by decantation, and the washing-waters may be used to dilute the sulphuric acid intended for new operations. This substitution of baryta for lime in the manufacture of tartaric acid has the advantages that the base employed is used in the form of artificial sulphate of baryta, and this sulphate separates from the tartaric acid with greater rapidity than sulphate of lime, which is very bulky, and is moreover very soluble in acid liquids.

Sulphuret of barium may be substituted for the native carbonate and the chloride; but the tartrate of baryta produced by this reaction has a gelatinous appearance and is washed with difficulty; whilst with the carbonate and chloride the tartrate is granulated and its washing is very easy. The only advantage that would be presented by the employment of the sulphuret would be its furnishing sulphuret, instead of chloride of potassium, the former being the more valuable.

Manufacture of citric acid.

The same process is applicable to this purpose, with the same advantages. Lemon-juice, concentrated or not, is converted into citrate of baryta by means of pulverized native carbonate, with the assistance of heat; the saturation being completed by means of a little sulphuret of barium, baryta precipitated by caustic soda, chloride of barium mixed with ammonia, or even by ammonia alone. These bodies precipitate the citrate retained in solution by an excess of citric acid. The citrate obtained may be purified by washing with cold water. Its decomposition must be effected with the aid of heat, by 1 equiv. of sulphuric acid of spec. grav. 1·834, diluted with 5 or 6 parts of water. To ascertain the quantity of sulphuric acid necessary for the decomposition of the citrate of baryta (and also of the other barytic salts here mentioned), a known quantity should be incinerated with the addition of a little pure nitrate of potash, and the amount of baryta determined.

The citric acid thus isolated, crystallizes with much greater facility than when citrate of lime is decomposed by sulphuric acid; in the latter case the citric acid retains some sulphate of lime.

Manufacture of acetic acid.

When crude pyroligneous acid is saturated with native carbonate of baryta or sulphuret of barium, it furnishes an acetate which should be calcined at a moderate temperature, to avoid decomposing it, but sufficiently to cause its solution to deposit the tarry matter. In all cases it is necessary in this calcination to keep below a red heat. This operation may, if necessary, be repeated several times.

The acetate of baryta thus obtained is decomposed by 1 equiv. of sulphuric acid; the decomposition is only complete when the solution of the acetate is not too much concentrated. The result is artificial sulphate of baryta and weak acetic acid, which, however, is strong enough to be applied in various ways in the arts. Thus it may be employed directly in the manufacture of white lead, acetate of lead, and other acetates.

When the solution of acetate of baryta is too concentrated, the sulphate of baryta does not separate in the ordinary form; it then retains some acetic acid, and presents a gelatinous, semitransparent appearance, which is not got rid of without difficulty.

To obtain a purer acid the acetate of baryta may be converted into acetate of soda, by the addition of sulphate of soda. In this way the formation of the double sulphate of soda and lime, which usually occurs in the ordinary process with lime, is avoided.

Chromic acid, hydroferrocyanic acid, &c.

Döbereiner had employed baryta in the preparation of chromic acid, and Porret in that of hydroferrocyanic acid.

I. The usual process employed in the laboratory for the isolation of chromic acid, consists in the action of an excess of sulphuric acid upon chromate of potash. To prepare this acid for use in the arts,

the author employs chloride of barium and neutral chromate of potash, the double decomposition of which furnishes chloride of potassium and chromate of baryta. The latter is treated with 1 equiv. of sulphuric acid, diluted with ten times its volume of water, and the action is aided by heat; the insoluble sulphate of baryta is rapidly deposited and the solution of chromic acid marks 10° B. The chromic acid may be concentrated to 50° or 60° B. by evaporation in earthenware vessels, or even in leaden cauldrons. The sulphate of baryta, even when washed, retains some chromic acid; it may be used in the preparation of colours.

Chromate of baryta may be substituted for chromate of lead in painting; it is of a bright yellow colour, but less intense than that of chromate of lead. Its economy and inalterability give it a preference over the lead-salt.

II. Ferrocyanide of barium, obtained by decomposing a hot solution of ferrocyanide of potassium by chloride of barium, is very sparingly soluble; it is precipitated at the moment when the solutions are mixed, in the form of small yellow crystals. In this state it still retains some potassium, from which it may be freed by boiling with a solution of chloride of barium.

By mixing together in the cold equivalent proportions of the ferrocyanide thus purified and dilute sulphuric acid, the decomposition takes place instantaneously; sulphate of baryta is thrown down, and the liquid, which acquires a green colour, contains the hydroferrocyanic acid. By using sulphuric acid of spec. grav. 1·834, diluted with 5 or 6 times its volume of water, the acid isolated presents a density of 12° to 15° B.

This acid cannot be concentrated by heat; to obtain it directly in a state of greater concentration, less water may be employed in its preparation, but then the sulphate of baryta would be washed with more difficulty. The acid should be preserved in well-stoppered earthen vessels.

With the acid thus isolated the author obtains hydroferrocyanic acid in a solid state and perfectly pure, by adding an excess of concentrated muriatic acid and a little æther, and drying the product without heat in presence of fragments of quicklime. In this way he avoids the presence of the chloride of potassium which remains mixed with the acid, when ferrocyanide of potassium is treated by the same agents.

This process is also applicable to all the acids which are now isolated by the decomposition of their lead-compounds by sulphuretted hydrogen, or their lime-compounds by sulphuric acid, such as malic acid, phosphoric acid, &c.—*Comptes Rendus*, November 2, 1858, p. 674.

Chemical Matches without Phosphorus or other Poison.
By M. Canouil.

The new matches are absolutely without white or red phosphorus, ordinary or amorphous. They cannot be used as a poison, and

when reduced to their least degree of inflammability give rise to no danger of fire. They are formed essentially of chlorate of potash, mixed with a small quantity of a metallic peroxide, bichromate or oxysulphuret, when it is desired to render them more inflammable. The author has found means to triturate the chlorate of potash, even when dry, without danger of explosion.

The new matches diffuse no odour, either in the manufacture or in use; they light without explosion or projection.—*Comptes Rendus*, June 28, 1858, p. 1268.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Note "On the Formation of the Peroxides of the Radicals of the Organic Acids." By B. C. Brodie, F.R.S.

The researches of Gerhardt showed the close resemblance which exists between the monobasic organic acids and the metallic protoxides. We have the chloride of acetyle corresponding to the chloride of the metal, and the hydrated and anhydrous acetic acid corresponding to the hydrated and anhydrous oxide. These investigations have been succeeded by others, which have had their origin in the consistent development of these ideas. The following discovery extends and completes these analogies. I have to add a new term to this series, of which hitherto no analogue has existed. This term is the peroxide of the organic radical,—the body which in the series of acetyle corresponds to the peroxide of hydrogen or barium in the series of the metal. Of these remarkable substances I have prepared two,—the peroxides of benzoyle and of acetyle; but the method by which these are procured is doubtless of extensive application, and we may consider ourselves as in possession of a class of bodies of a new order, the study of which cannot fail greatly to extend our knowledge.

These peroxides are prepared by the action of the anhydrous acid, or the corresponding chloride, upon the peroxide of barium. It is first necessary to prepare this peroxide in a pure condition. This is effected by precipitation of the solution of the peroxide of barium in hydrochloric acid by baryta water, and by drying *in vacuo* the precipitate thus obtained. The peroxide of barium thus procured is perfectly pure, with the exception of a trace of carbonate. In appearance it resembles magnesia.

To prepare the peroxide of benzoyle, the chloride of benzoyle and the peroxide of barium are taken in equivalent proportions and mixed in water. A mutual decomposition takes place; and a substance is formed which, after crystallization from anhydrous ether, gave the following results to analysis:—

Carbon	69·23
Hydrogen	4·10
Oxygen	26·67
	100·00

The calculated numbers for the peroxide of benzoyle are

C_{14}	168	69·42
H_{10}	10	4·13
O_4	64	26·45
	242	100·00

This substance contains an atom of oxygen more than the anhydrous acid, and (reducing the formula to its simplest expression) one atom of hydrogen less than the hydrated acid. Thus we have $C_{14} H_{10} O_3$ anhydrous benzoic acid, $C_{14} H_{10} O_4$ peroxide of benzoyle, and $C_7 H_6 O_2$ hydrated benzoic acid, $C_7 H_5 O_2$ peroxide of benzoyle, as we have H_2O water, and $H_2 O_2$ or HO for the peroxide of hydrogen. This body crystallizes from ether in large and brilliant crystals. Heated a little above the boiling-point of water, it decomposes, with a slight explosion and the evolution of carbonic acid. Boiled with a solution of potash, it is resolved into oxygen gas and benzoic acid.

The peroxide of acetyle is prepared by mixing anhydrous acetic acid and peroxide of barium, in equivalent proportions, in anhydrous ether. The mixture is to be effected very gradually, being attended with evolution of heat. The ether, after filtration from the acetate of baryta produced, is to be carefully distilled off at a low temperature, and the fluid which remains washed with water. After three or four washings, the water ceases to be acid, and a viscid liquid remains, which is the peroxide of acetyle. This substance possesses the following properties:—It is extremely pungent to the taste; the smallest portion of it placed upon the tongue burns like cayenne pepper. The substance suspended in water immediately decolorizes a solution of sulphate of indigo. It instantly peroxidizes the protoxide of manganese, and converts the yellow prussiate of potash into the condition of red prussiate. Baryta-water poured upon the substance is converted to the condition of peroxide of barium, with formation of acetate of baryta. Lastly, a single drop of the substance itself, placed on a watch-glass and heated, explodes with a loud report, shivering the glass to atoms.

To analyse the peroxide of acetyle, I availed myself of its decomposition by baryta-water. An undetermined quantity of the substance was thus decomposed, and the oxygen estimated which was evolved by the decomposition of the peroxide of barium formed, by platina-black, and the acetate of baryta determined as sulphate. The result is the same as though the peroxide of acetyle were decomposed into anhydrous acetic acid and oxygen, thus,

$$C_4 H_6 O_4 = C_4 H_6 O_3 + O.$$

Thus for every 16 parts of oxygen evolved, 2 equivalents of acetate of baryta and 1 of sulphate of baryta, $SO_4 Ba_2$, would be produced. Now we have

$$\begin{array}{cccccc} SO_4 Ba_2 & & O & & & \\ 233{\cdot}2 & : & 16 & :: & 100 & : \quad 6{\cdot}86. \end{array}$$

In the actual experiment 1·776 gr. of sulphate of baryta was obtained, and 0·1225 of oxygen evolved.

1·776 : 0·1225 :: 100 : 6·89.

It has not yet been in my power to pursue further the study of these substances. I may, however, observe, that the peroxide of acetyle contains the elements of carbonic acid and of the acetate of methyle, and the peroxide of benzoyle the elements of carbonic acid and of the benzoate of phenyle. I have ascertained that the peroxide of benzoyle, when carefully heated, loses exactly one equivalent of carbonic acid; but the substance formed, although isomeric with the benzoate of phenyle, has not the properties of that body. It is a yellow resin, soluble in ether and alkalies, from which latter solution it is precipitated by acids.

The existence of a hydrated peroxide may be anticipated, intermediate between the organic peroxide and the peroxide of hydrogen, in the same sense as the organic acid is intermediate between water and the anhydrous acid. This substance in the series of benzoyle would be isomeric with salicylic acid. My efforts, however, to procure these bodies have, as yet, been unsuccessful; and it is to be remembered that we have no evidence of the existence of a hydrated peroxide of barium, or of any other metal, corresponding to the hydrated protoxide. In the series of ethyle the diatomic alcohol of Wurtz ($C_2 H_8 O_2$) is isomeric with the hydrated peroxide. But the true peroxide of ethyle remains yet to be discovered.

The question naturally arises as to what would be the result of making similar experiments with the chlorides and the anhydrides of the bibasic acids. Now carbonic acid may be regarded as the peroxide of oxalic acid: it is the constant product of the action of oxidizing agents upon that body; and were we able to procure the unknown anhydride of oxalic acid, it would not be an unreasonable anticipation that with the peroxide of barium it would decompose into oxalate and carbonic acid, thus

$$2 C_2 O_3 + Ba_2 O_2 = C_2 O_4 Ba_2 + 2CO_2.$$

A similar experiment with anhydrous succinic acid would produce succinate of baryta and a homologue of carbonic acid, the existence of which is also indicated by other considerations. It is premature to dwell upon this point; but in this direction also I have made some experiments.

"Notice of Researches on the Sulphocyanide and Cyanate of Naphtyle, conducted by Vincent Hall, Esq." By A. W. Hofmann, Ph.D., F.R.S. &c.

The transformation of phenylcarbamide and phenylsulphocarbamide under the influence of anhydrous phosphoric acid, respectively into cyanate and sulphocyanide of phenyle, an account of which I submitted to the Society several months ago, suggested the probability that the hitherto unknown cyanates and sulphocyanides of radicals similar to phenyle might be obtained by analogous processes.

To establish this point experimentally, Mr. Vincent Hall has examined, in my laboratory, the deportment of some of the deriva-

tives of *naphtylamine* under the influence of agents capable of fixing ammonia and its analogues.

Mr. Hall has found that the crude naphtaline, such as it is obtained from the gas-works, submitted at once, without sublimation, to the action, first of fuming nitric acid, and subsequently of acetic acid and metallic iron, furnishes the naphtylamine sufficiently pure for these experiments. The crude product thus obtained was digested with bisulphide of carbon in order to convert it into *naphtylsulphocarbamide.*

By distilling naphtylsulphocarbamide with anhydrous phosphoric acid, Mr. Hall has obtained a beautiful crystalline compound of a faint but peculiar odour, readily fusible, easily soluble in alcohol and ether, insoluble in water.

The analysis of this compound has led to the formula

$$C_{22}H_7NS_2 = C_{20}H_7, C_2NS_2,$$

showing that it is in fact *sulphocyanide of naphtyle,* formed according to the equation:—

$$\left.\begin{matrix}(C_2\ S_2)''\\ (C_{20}\ H_7)_2\\ H_2\end{matrix}\right\} N_2 = C_{20}\left.\begin{matrix}H_7\\ H_2\end{matrix}\right\} N + C_{20}H_7, C_2NS_2.$$

Boiled with an alcoholic solution of naphtylamine, this compound readily reproduces naphtylsulphocarbamide, which by its insolubility is easily distinguished and separated from the sulphocyanide.

Gently heated with phenylamine, the new sulphocyanide gives rise to the formation of a crystalline compound, of properties very similar to those of the naphtylsulphocarbamide. This new body is *phenyl-naphtyl-sulphocarbamide**, containing—

$$C_{34}H_{14}N_2S_2 = C_{12}H_5, \left.\begin{matrix}(C_2\ S_2)''\\ C_{20}\ H_7\\ H_2\end{matrix}\right\} N_2.$$

Naphtylcarbamide, as obtained by the action of potassa on the corresponding sulpho-compound, or by the distillation of oxalate of naphtylamine, is likewise powerfully attacked by anhydrous phosphoric acid. Among the products of distillation a compound is found, which, by its chemical properties, is readily identified as *cyanate of naphtyle,*

$$C_{22}H_7NO_{20} = C_2H_7, C_2NO_2,$$

although the small quantity in which this body is produced—by far the greater amount of the naphtylcarbamide being charred by the action of anhydrous phosphoric acid—has hitherto prevented Mr. Hall from fixing the nature of the compound by an analysis.

* By the action of sulphocyanide of phenyle upon naphtylamine, I have obtained a crystalline compound very similar in its general characters to the body which Mr. Hall procures by the action of sulphocyanide of naphtyle on phenylamine. This substance likewise contains

$$C_{34}H_{14}N_2S_2 = C_{12}H_5, \left.\begin{matrix}(C_2\ S_2)''\\ C_{20}\ H_7\\ H_2\end{matrix}\right\} N_2,$$

for

$$C_{12}H_5H_2N + C_{20}H_7C_2NS_2 = C_{20}H_7, H_2N + C_{12}H_5, C_2NS_2 = C_{34}H_{14}N_2S_2.$$

Are these two bodies identical, or only isomeric? [A.W.H.]

INDEX TO VOL. XVI.

ACEDIAMINE, preparation and constitution of, 85.
Acetal, conversion of aldehyde into, 461.
Acetamide, compounds of, 84.
Acetic acid, conversion of, into methylic alcohol, 445; manufacture of, 473.
Acetones, on the constitution of the, 64.
Acids, on the determination of several mineral, 237.
——, bibasic, of the series $C^nH^{n-2}O^8$, 247.
Æthers, hydrosulphuric, compounds of, with biniodide of mercury, 466.
Æthyle, on the action of the alkalies upon sulphocyanide of, 236.
Æthylydene, on the oxychloride of, 215.
Albumen, oxidation of, by permanganate of potash, 101.
Alcoholic fermentation, on the theory of, 61, 69, 126, 369.
Aldehyde, researches upon, 215; on the constitution of, 267; on the compound of, with anhydrous acetic acid, 305; conversion of, into acetal, 461.
Aldehyde-ammonia, on, 136.
Alexander, J. H., on the commercial varieties of brown sugar, 151.
Alkalimeter, on a modification of Mohr's, 255.
Alkaloids, vegetable, on the sulphuric derivatives of the, 405.
Alloxane, on the action of hydrocyanate of ammonia upon, 91.
Alumina, on the use of hydrate of, in the analysis of vegetable constituents, 95; separation of, from oxide of iron, 274; carbonate of, 411.
Aluminium, on iodide, bromide, and chloride of, 269; equivalent of, 385; double chlorides of, 444.
Amides of phosphoric acid, 87.
Aminocobalt, action of sulphurous acid and the sulphites upon sesquioxide of, 204.
Ammonio-oxide of copper, a solvent for vegetable fibre, 66.
Amyle, 209.
Amyloglycol, 129.
Anchoic acid, identity of, with lepargylic acid, 301.
Angostura bark and its essential oil, on, 192.
Aniline, action of nitrous acid on, 120; action of chloroform upon, 259; action of bromide of ethylene on, 373; action of bichloride of carbon on, 378.
Anilotic acid, identity of, with nitrosalicylic acid, 284.
Antimony, on the molecular properties of, 59; separation of, from arsenic, 311; on the properties of electro-deposited, 354.
Arsenic, on the discrimination and separation of, from antimony and tin, 311.
Arsenio-methylic compounds, on the, 253.
Arsenites, action of air on alkaline, 121.
Atacamite, artificial formation of, 430.
Atropine, valerianate of, 68.
Babo, Prof. von, on piperic acid, 7, 241; on some decompositions of cinchonine, 49; on aldehyde-ammonia, 136.
Barium, equivalent of, 141; on the action of sulphuric acid upon the compounds of, 446.
Baryta, determination of, 19; industrial applications of, 406, 471.
Basset, M., on the clarification of sugars, 96.
Bauer, Dr. A., on the preparation of the monosulphuret of potassium, 468.
Bäyer, A., on the arsenio-methylic compounds, 253.
Berthelot, M., on the synthesis of wood-spirit, 33; on the transformation into sugar of various immediate principles in the tissues of invertebrate animals, 361; on melezitose, 388; on the synthesis of the hydrocarbons, 401, 427; on trehalose, 464.
Bile, action of, upon fats, 356.
Bill, J. W., on a test for cinchonine, 335; on the molybdate of ammonia test for phosphoric acid, 373.
Binitrophloretic acid and salts, 25.
Blowpipe, new fluid for the, 36.
Boghead coal, products of the destructive distillation of, 119, 183, 207, 285,

Bolley, P., on the products of the action of chlorine upon paraffine, 303; on a new ferrocyanide of potassium and copper, 326; on a condition under which the silicates of the alkaline earths are tolerably soluble, 347; on the preparation of laurostearine and lauric acid, 368.
Boracic acid, behaviour of, to tartaric acid, 190.
Boron and its affinities, investigation of, 1; behaviour of, to nitric oxide, 263.
Brain, chemical constituents of the, 35.
British Association, proceedings of the, 410.
Brodie, B. C., on the formation of the peroxides of the radicals of the organic acids, 475.
Bromine, action of, upon fulminating mercury, 232.
Brüning, A., on lactic acid, 196; on a new product of the decomposition of iodoform with potash, 216; on the preparation of tetræthylurea, 227; on the action of the alkalies upon sulphocyanide of æthyle, 236.
Brunner, Prof. C., on the preparation of manganese, 5, 178; on the testing of milk, 277; on a process for decolorizing the fatty oils, 338.
Buckton, G. B., on the isolation of mercuric methyle, 117; on the identity of anchoic acid with lepargylic acid, 301; on the isolation of mercuric, plumbic, and stannic ethyle, 415.
Buff, H., on some new compounds of silicium, 23.
Bunsen, R., on the preparation of pure compounds of cerium, 181; on the oxides of cerium, 221; on the discrimination and separation of arsenic from antimony and tin, 311.
Butyle, 207.
Cadmium, salts of, 271.
Caffeine, amount of, in coffee-beans, 252.
Cahours, A., on some new derivatives of oil of cloves, 133.
Calcium, preparation of, 329.
Canouil, M., on chemical matches without phosphorus, 474.
Caprylic alcohol, 130.
—— aldehyde, 130.
Carameline, preparation and properties of, 177.
Carbonate of potash, on a new method of obtaining, from felspar and similar minerals, 37.
Carminic acid, 64.
Casselmann, Dr. A., on franguline, 108.
Cellulose, solubility of, in ammoniacal solution of copper, 336.
Cerium, preparation of pure compounds of, 181; on the oxides of, 221.
Chinese yellow-pods, on the, 128.
Chitine, conversion of, into sugar, 361.
Chloral, compounds of, 405.
Chloralide, formation of, 405.
Chlorophloretic acid, 29.
Chromate of lead, preparation of, 319.
—— of potash, on some applications of the, in metrical analysis, 19.
Chromates of mercury, 390.
Chromic acid, determination of, 20; compounds of, with oxide of mercury, 324; on, 473.
Chromic oxide, on the carbonate of, 411.
Chromium, on the sesquiphosphate of, 220.
—— and aluminium, on a crystallized compound of, 294.
Cinchona alkaloids, researches on the, 56, 437.
Cinchonine, on some decompositions of, 49, 89; new derivatives of, 327; test for, 335; on the benzoic derivatives of, 426.
Citric acid, on the manufacture of, 472.
Cloez, S., on a new mode of treating speiss and copper-nickel, 154; on the various states of sulphur as separated from its combinations, 229; on the employment of permanganate of potash for the determination of sulphur in gunpowder and sulphuretted compounds, 393.
Cochineal, researches on, 63.
Copper, determination of, 138, 370; behaviour of, in hydrochloric gas, 310; ferrocyanide of potassium and, 326.
Copper-nickel, on a new mode of treating, 154.
Cotton, method of distinguishing from silk, 372.
Cotton-printing, fixation of metallic sulphurets in, 339.
Creatine, simple mode of preparing, 149.
Crisine, preparation and properties of, 51.
Crocine, 332; crocetine, 332.
Croft, H., on the action of air on alkaline arsenites, 121.
Croton oil, on, 272.
Crotonic acid and salts, 272.
Cusparine, 192.
Debray, H., on the action exerted by the mixture of an oxidizing and a reducing body upon the metals and their oxides, 67; on molybdenum, 366.

Debus, Dr. H., on the action of ammonia on glyoxal, 352.
Dessaignes, M., on a new acid obtained by the oxidation of malic acid, 341.
Deville, H. Sainte-Claire, on boron and its affinities, 1.
Diamides, on the, 358.
Dowling, J., on the deportment of phosphate of sesquioxide of chromium with ammonia and other reagents, 220.
Dried yeast and its adulteration, 240.
Drion, C., on the reaction of perchloride of phosphorus upon the essential oil of *Gaultheria procumbens*, 448.
Dumas, M., on the equivalents of the elements, 174.
Elayle, on the constitution of protochloride of, 267, 461.
Enodyle, preparation and properties of, 160.
Equivalents of the elements, on the, 174.
Essential oil of China oranges, 3.
Ethyle, preparation of the iodide of, 452.
Ethyle-compounds, on some, containing the alkali-metals, 455.
Eugenic acid, constitution of, 170.
Excretine, observations on, 357.
Fats, action of bile upon, 356.
Fatty oils, process for decolorizing the, 338.
Fehling, H., on the quantitative determination of sugar, 297.
Ferric oxide, on the carbonate of, 412.
Fibre, woody, solubility of, in ammoniacal solution of copper, 336.
Field, F., on cupreous oxide of manganese from Chile, 104; on the artificial formation of oxychloride of copper (atacamite) and the sulphates of copper, 430.
Fluorine, on the diffusion of, 199.
Franguline, on, 108.
Frankland, Dr. E., on sodium-ethyle and potassium-ethyle, 459.
Frapoli, M., on the conversion of aldehyde into acetal, 461.
Frerichs, F. T., on the occurrence of urea, taurine, and scyllite in Plagiostomous fishes, 281.
Fresenius, R., on the determination of nitric acid, 299; on the solubility of sulphate of strontia in nitric, muriatic, and acetic acids, 338.
Friedel, C., on the constitution of the acetones, 64; on the conversion of acetic acid into methylic alcohol, 445.
Fritzsche, J., on compounds of hydrocarbons with picric acid, 193; on the action of nitric acid upon phenic acid, 224.
Fulminating mercury, action of bromine upon, 232.
Gardenia grandiflora, on the yellow colouring matter of the fruit of, 331.
Gases, on the measurement of, in analysis, 256.
Gélis, A., on the products furnished by sugar and starch when heated, 176.
Gentele, J. G., on the manufacture of ultramarine, 14.
Genth, F. A., on a new base containing osmium and the elements of ammonia, 198.
Geuther, Dr. A., on the constitution of aldehyde and protochloride of elayle, 267; on the compound of aldehyde with anhydrous acetic acid, 305; on some compounds of chromic acid with oxide of mercury, 324, 390.
Gibbs, W., on a new base containing osmium and the elements of ammonia, 198.
Gilbert, Dr. J. H., on the annual yield of nitrogen per acre in different crops, 410.
Gladstone, Dr. J. H., on the chemical action of water on soluble salts, 97.
Glucosides, on the action of human saliva upon, 148.
Glycogene, preparation and composition of, 293.
Glycogenous matter of the liver, on the, 293.
Glycolic acid, formation of, from acetic acid, 261.
Glycosine, constitution of, 353.
Glyoxal, action of ammonia on, 352.
Glyoxaline, preparation of, 353.
Gore, G., on the molecular properties of antimony, 59, 354.
Grape-sugar, reagent for, 280.
Guanine, compounds of, with hydrobromic and hydriodic acids, 135.
Guano, Peruvian, on volatile bases and acids in, 117.
Guignet, E., on the employment of permanganate of potash for the determination of sulphur in gunpowder and sulphuretted compounds, 393.
Gunpowder, determination of sulphur in, 393.
Hallwachs, Dr. W., on the origin of the hippuric acid in the urine of the Herbivora, 201.
Hanhart, M., on some new æthers of stearic and margaric acids, 383.
Hauer, Carl von, on the equivalent of manganese, 41; on the composition of the bromides of potassium and tellurium, and the equivalent of tellurium, 81.

Heintz, Prof., on the preparation and on some new compounds of saccharic acid, 449.
Hempel, C. W., on the detection of small quantities of metallic iodides, 218.
Henry, O., on the detection of iodine by starch, 371.
Herapath, Dr. W. B., on the cinchona alkaloids, 56, 70, 437.
Herzog, Dr. C., on Angostura bark and its essential oil, 192.
Hippuramide, preparation and properties of, 52.
Hippuric acid, compounds of, 31; on the origin of the, in the urine of the Herbivora, 201.
Hlasiwetz, Prof. H., on phloretic acid, 9, 25; on new products of decomposition of bodies of the uric acid group, 94.
Hofmann, Dr. A. W., on the poly-ammonias, 155, 259; on the diamides, 358; on the action of bromide of ethylene upon aniline, 373; on the action of bichloride of carbon upon aniline, 378; researches on the phosphorus-bases, 395; on the action of bisulphide of carbon on triethylphosphine, 398; on the history of the monamines, 434.
Hops, process for distinguishing sulphured, 180.
Humbert, E., on the detection of iodine by starch, 371.
Hunt, T. S., on some reactions of the salts of lime and magnesia, 320.
Hydrocarbons, synthesis of the, 401.
Hydroferrocyanic acid, on, 473.
Hyposulphuric acid, on the constitution of, 200.
Iodides, detection of minute quantities of soluble metallic, 218.
Iodine, test for, 279; detection of, by starch, 371; detection of, in nitric acid and nitrate of soda, 452.
Iodoform, on a new product of the decomposition of, with potash, 216.
Iron, on the behaviour of perchloride of, to hydriodic acid, 279.
——, cast, on the action of carbonate of soda upon, at high temperatures, 16.
—— ores, on the analysis of, 274.
Isomeric bodies, on, 133.
Jacquemin, E., on some compounds of hippuric acid, 51; on the action of aqueous vapour and oxide of carbon upon some sulphates, 406; on the action of sulphuric acid upon the compounds of barium, strontium, and calcium, 446.
Kawalier, M., on the tannine of galls, 421.
Kekulé, M., on the action of bromine upon fulminating mercury, 232; on the formation of glycolic acid from acetic acid, 261; on the glycogenous matter of the liver, 293.
Keller, E., on piperic acid, 7, 241.
Keller, Dr. F., on scammony, 106.
Kerner, D. G., on compounds of guanine with hydrobromic and hydriodic acids, 135.
Kessler, L., on the preparation and analysis of oxide of uranium, 319.
Kieffer, L., on some reactions of morphia, 54.
Knop, Dr. W., on the behaviour of molybdate of ammonia to silicic acid, 13; on a fat containing phosphorus, in peas, 369.
Kœne, C. J., on the constitution of hyposulphuric acid, 200.
Kuhlmann, F., on the industrial applications of baryta, 406, 471.
Künzel, Dr. Carl, on the action of sulphurous acid and the sulphites upon sesquioxide of aminocobalt, 204.
Lactic acid, on, 196; on the constitution of, 441.
—— —— of flesh, on the conversion of, into ordinary lactic acid, 330.
Lactic fermentation, on the so-called, 21.
Lauric acid, preparation of, 368.
Laurostearine, preparation of, 368.
Lawes, J. B., on the annual yield of nitrogen per acre in different crops, 410.
Lead, determination of, 19; equivalent of, 167; alloys of, 296.
Leconte, M., on the estimation of urea, 432.
Lenssen, E., on the compounds of oxalic acid with metallic oxides, 48, 264.
Lepargylic acid and salts, 248; identity of anchoic acid with, 301.
Lieben, A., on aldehyde, 215.
Liès-Bodart, M., on the preparation of calcium, 329; on the action of sulphuric acid upon the compounds of barium, strontium, and calcium, 446.
Lime, on some reactions of the salts of, 320; and salts of, solubility of, in sulphuric acid, 448.
Limpricht, H., on the preparation of œnanthylene from œnanthole, 115.
Lipic acid, properties and composition of, 250.
Literary and Philosophical Society of Manchester, proceedings of, 18.
Liver, on the glycogenous matter of the, 293.

Loir, A., on compounds of the hydrosulphuric æthers with biniodide of mercury, 466.
Löwenthal, J., on a sensitive reagent for grape-sugar, 280.
Luca, S. de, on the essential oil of China oranges, 3.
Lucius, E., on volatile bases and acids in Peruvian guano, 117.
Magnesia, on some reactions of the salts of, 320.
Malonic acid, preparation and constitution of, 341.
Manganese, preparation of, 5, 178; equivalent of, 41; cupreous oxide of, 104; siliciuret of, 233.
Mannite, combinations of, with lime, baryta, and strontia, 53.
Marcet, Dr. W., on the action of bile upon fats and on excretine, 356.
Margaric acid, new æthers of, 383.
Marignac, C., on the equivalents of barium, strontium, and lead, 141, 165.
Marsh, E., on pimelic acid and some of its compounds, 105.
Matches without phosphorus or other poison, 474.
Matthiessen, Dr. A., on the action of nitrous acid on aniline, 120.
Maumené, M., on the theory of alcoholic fermentation, 69.
Melezitose, 388.
Mendius, O., on sulphosalicylic acid and conjugate acids, 111.
Mène, C., on the drying and weighing of precipitates in chemical analyses, 431.
Merck, M., on veratric acid, 307.
Mercuric ethyle, 417.
—— methyle, on the isolation of, 117.
Mercury, on precipitated oxide of, 345.
Metals, on two new, from the Swedish magnetic iron ore, 169.
Methylophosphorous acid, 12.
Meyer, Dr. E., on a new method of obtaining carbonate of potash from felspar, 37.
Miette, M., on valerianate of atropine, 68.
Milk, new mode of analysing, 140; on the testing of, 277.
Mitscherlich, Prof., on mycose, 123.
Mohr, C., on the behaviour of perchloride of iron to hydriodic acid, 279.
Molybdate of ammonia, behaviour of, to silicic acid, 13.
—— —— test, on the, 373.
Molybdenum, on, 366; compounds of, with nitrogen, 163, 334.
Monamines, on the, 434.
Monier, E., on a new mode of analysing milk, 140.
Monotropa Hypopitys, on the occurrence of salicylate of methyle in, 200.
Morfit, C., on the commercial varieties of brown sugar, 151.
Morphia, on some reactions of, 54.
Mucklé, A., on the amount of platinum in the platinum residues, 161.
Müller, Dr. W., on the chemical constituents of the brain, 35.
Mycose, on, 123.
Nickel, ammoniacal solution of protoxide of, a means of distinguishing silk and cotton, 372.
Nicklés, J., on the diffusion of fluorine, 199.
Niobium, sulphuret and perfluoride of 469.
Nitric acid, determination of, 299; testing of, for iodine, 452.
Nitrofrangulic acid and salts, 109.
Nitrogen, on the annual yield of, per acre in different crops, 413.
Nitrophenic acid, 224.
Nitrosalicylic acid, identity of, with anilotic acid, 284.
Nitrosulphurets, on double, 127.
Nux vomica, on the alkaloids of, 467.
Œnanthylene, preparation of, from œnanthole, 115.
Oesten, F., on the separation of tantalic acid from the acids in the columbites, 179.
Oil of cloves, new derivatives of, 133.
Oil of *Gaultheria procumbens*, action of perchloride of phosphorus upon, 448.
Oleone, 351.
Organo-metallic radicals, on the, 415.
Osmium, on a new base containing, 198.
Oxalane, preparation and composition of, 92.
Oxalates, on some, 48, 264.
Painting with oxychloride of zinc, on a new process of, 239.
Parabanic acid, products of decomposition of, 94.
Paraffine, on some products of the action of chlorine upon, 303.
Pasteur, L., on the so-called lactic fermentation, 21; on alcoholic fermentation, 61, 126, 369; on the fermentation of tartaric acid, 228.
Payr, M. von, on saponine, 132.
Pearson, R.W., on some applications of the chromates of potash in metrical analysis, 19.
Pelosine, action of potash upon, 321.

Permanganate of potash, on the oxidizing properties of the, 236, 454.
Petersen, Dr. T., on some products of decomposition of sebacate of lime, 36.
Phenic acid, action of nitric acid upon, 224.
Phenyle, on cyanate and sulphocyanide of, 358.
Phipson, T. L., on a colouring matter from *Rhamnus frangula*, 344.
Phloretic acid and salts, 9, 25.
Phloretylamic acid, 29.
Phosphaminic acid, 87.
Phosphate of soda and lithia, composition of, 150.
Phosphoric acid, amides of, 87.
Phosphorus, on a fat containing, in peas, 369.
—— bases, researches on the, 395.
Phthalamine, 343.
Picric acid, on compounds of hydrocarbons with, 193.
Pimelic acid and compounds, 105.
Pinoline, 350.
Piperic acid and salts, 7, 241.
Piperine, on the decomposition of, by potash, 330.
Pisani, F., on a new fluid for the blowpipe, 36; on a new mode of determining copper, 370.
Platinum, on the amount of, in the platinum residues, 161.
—— bases, on some, 346.
Plumbic bis-ethyle, 418.
Plunkett, W., on a new test for potash, 217; on the deportment of phosphate of sesquioxide of chromium with ammonia and other reagents, 220.
Poly-ammonias, on the, 155, 259.
Polygonum Fagopyrum, on a yellow colouring matter from, 18.
Potash, new test for, 217.
Potassium, preparation of the monosulphuret of, 468.
Potassium-ethyle, on, 457, 459.
Precipitates, on the drying and weighing of, in chemical analyses, 431.
Pyrodextrine, preparation and properties of, 178.
Pyrogallic acid, researches on, 381.
Quinine, new derivatives of, 327; investigation of, 363; on the benzoic derivatives of, 426.
Rammelsberg, C., on the composition of phosphate of soda and lithia, 150.
Reischauer, C., on the amounts of sulphuretted hydrogen and hydrocyanic acid in tobacco-smoke, 364.
Rhamnoxanthine, on the nature and properties of, 344.
Rhamnus frangula, on a colouring matter from, 344.
Ricinoleic acid, products of decomposition of, 130.
Rochleder, Prof. F., on the use of hydrate of alumina in the analysis of vegetable constituents, 95; on the Chinese yellow-pods, 128; on the yellow colouring matter of *Gardenia grandiflora*, 331.
Rose, H., on the behaviour of boracic acid to tartaric acid, 190; on the combination of nitrate of soda with nitrate of silver, 200; on the sulphuret and perfluoride of niobium, 469.
Rose-water, artificial, 352.
Rosing, A., on the action of hydrocyanate of ammonia upon alloxane, 91; on pyrogallic acid, 381.
Rosolic acid, derivation and composition of, 20.
Roussin, M., on double nitrosulphurets, 127.
Royal Society, proceedings of the, 56, 70, 97, 117, 155, 256, 352, 373, 395, 415, 434, 455, 475.
Rue, on the constitution of the essential oil of, 159.
Russell, Dr. W. J., on the measurement of gases in analysis, 256.
Rutine, 18.
Sacc, Dr. H., on the fixation of the metallic sulphurets in cotton-printing, 339.
Saccharic acid, preparation and new compounds of, 449.
Saint-Gilles, Péan de, on the oxidizing properties of the permanganate of potash, and on the determination of several mineral acids, 236, 454.
Salicylate of methyle, on the occurrence of, in *Monotropa Hypopitys*, 200.
Saliva, on the action of human, upon glucosides, 148.
Saponine, on, 132.
Scammonic acid, 106.
Scammonolic acid, 107.
Schiff, Dr. H., on methylophosphorous acid, 12; on the amides of phosphoric acid, 87; on salts of cadmium, 251.
Schischkoff, L., on the action of hydrocyanate of ammonia upon alloxane, 91.
Schlagdenhauffen, M., on some compounds of hippuric acid, 51.
Schlippe, T., on croton oil, 272.
Schlossberger, Prof., on Schweizer's test, 336; on a means of distinguishing silk and cotton, 372.

Schunck, Dr., on a yellow colouring matter obtained from the leaves of the *Polygonum Fagopyrum*, 18.
Schutzenberger, P., on cochineal, 63; on two new derivatives of quinine and cinchonine, 327; on phthalamine, 343; on quinine, 368; on strychnine, 386; on the sulphuric derivatives of the vegetable alkaloids, 404; on the benzoic derivatives of quinine, cinchonine, and strychnine, 426; on the alkaloids of nux vomica, 467.
Schweizer, Dr. E., on a solvent for vegetable fibre, 66, 336.
Scyllite, on the occurrence of, in Plagiostomous fishes, 281.
Sebacate of lime, products of decomposition of, 86.
Sebacine, constitution of, 87.
Selenium and aluminium, on the double chloride of, 444.
Silicates of the alkaline earths, on the solubility of the, 347.
Silicic acid, behaviour of molybdate of ammonia to, 13.
Silicium, new compounds of, 23; on the presence of oxide of, in the residue on dissolving pig-iron, 173.
Silk, behaviour of, towards ammoniacal solution of copper, 337; method of distinguishing from cotton, 372.
Slater, J. W., on a modification of Mohr's alkalimeter, 255; on alloys of zinc, tin, and lead, 296.
Smith, R. A., on the derivation and composition of rosolic acid, 20.
Sodium-ethyle, on, 456, 459.
Sorel, M., on a new process of painting with oxychloride of zinc, 239.
Souchay, A., on the compounds of oxalic acid with metallic oxides, 48.
Speiss, on a new mode of treating, 154.
Städeler, G., on caprylic aldehyde and caprylic alcohol, 130; on the action of human saliva upon glucosides, 148; on the occurrence of creatine, and a simple mode of preparing it, 149; on the occurrence of urea, taurine, and scyllite in the organs of the Plagiostomous fishes, 281; on the detection of uric acid, 334; on some compounds of chloral, and the formation of chloralide, 405.
Städeler, S., on the oxidation of albumen by permanganate of potash, 101.
Stannethyles, on the, 271, 419.
Stannic bis-ethyle, 419.
Starch, on the products furnished by, when heated, 177.
Stearic acid, new æthers of, 383.
Stein, Prof., on the testing of nitric acid and nitrate of soda for iodine, 452.
Stibæthyle, on the constitution of, 270.
Strecker, A., on compounds of acetamide, 84; on the constitution of the compounds of stibæthyle and the radicals of stannæthyle, 270; on the identity of nitrosalicylic acid with anilotic acid, 284; on the conversion of the lactic acid of flesh into ordinary lactic acid, 330; on the decomposition of piperine by potash, 330.
Strontia, solubility of sulphate of, in nitric, muriatic, and acetic acids, 338.
Strontia and salts, solubility of, in sulphuric acid, 447.
Strontium, equivalent of, 165.
Strychnine, investigation of, 386; on the benzoic derivatives of, 426.
Sugar, on the products furnished by, when heated, 176; estimation of, 297; formation of, from the tissues of invertebrate animals, 361.
Sugars, chemical examination of the commercial brown, 151; clarification of, on the, 96.
Sulphocinchonic acid, 404.
Sulphoquinic acid, 404.
Sulphosalicylic acid and salts, 111.
Sulphur, on the various states of, 229; determination of, 393.
Sulphuric acid, testing of, for nitric and hyponitric acids, 199; manufacture of, 406.
Tannine of galls, on the, 421.
Tantalic acid, separation of, from the acids in the columbites, 179.
Tartaric acid, on the fermentation of, 228; on the manufacture of, 472.
Taurine, on the occurrence of, in Plagiostomous fishes, 281.
Tellurium, equivalent of, 81; composition of the double bromide of potassium and, 83; and aluminium, on the double chloride of, 444.
Terriel, A., on the determination of copper, 138.
Tetræthylurea, preparation of, 227.
Tin, alloys of, 296; separation of, from arsenic, 311.
Tissier, C., on the action of carbonate of soda upon cast iron at high temperatures, 16; on the equivalent of aluminium, 385.
Tobacco-smoke, on the amounts of sulphuretted hydrogen and hydrocyanic acid in, 364.

Trehalose, properties and composition of, 464.
Triethylphosphine, 396; action of bisulphide of carbon on, 398.
Trimethylamine, action of bibromide of ethylene on, 434.
Tungsten, on the nitrurets of, 334.
Tunicine, conversion of, into sugar, 361.
Ubaldini, J., on combinations of mannite with lime, baryta, and strontia, 53.
Ullgren, Prof., on two new metals in the Swedish magnetic iron ore, 169.
Ultramarine, manufacture of, 14.
Uranium, preparation and analysis of oxide of, 319; double acetates of, 390.
Urea, on the occurrence of, in the organs of the Plagiostomous fishes, 281; estimation of, 432.
Uric acid, detection of, 334.
—— —— group, new products of decomposition of bodies of the, 94.
Urlaub, E., on compounds of molybdenum with nitrogen, 163; on compounds of vanadium with nitrogen, 197.
Valerianate of atropine, on, 68.
Vanadium, compounds of, with nitrogen, 197.
Vapour-densities, new method of taking, 213.
Vegetable constituents, on the use of hydrate of alumina in the analysis of, 95.
—— fibre, on a solvent for, 66, 336.
Veratric acid, investigation of, 307.
Vincent, A., on the testing of sulphuric acid for nitric and hyponitric acids, 199.
Vogel, Prof. A., jun., on the amount of caffeine in coffee-beans, 252; on the amounts of sulphuretted hydrogen and hydrocyanic acid in tobacco-smoke, 364.
Vohl, Dr. H., on the preparation of chromate of lead for use in elementary analyses, 319; on pinoline and oleone, 350.
Vrij, Dr. De, on iodide of ethyle, 452.
Wagner, Prof. R., on a process for distinguishing sulphured hops, 180; on artificial rose-water, 352.
Wallace, W., on the analysis of hæmatite and magnetic iron ores, and the separation of oxide of iron from alumina, 274; on precipitated oxide of mercury, 345; on the carbonates of alumina, chromic oxide, and ferric oxide, 410.
Wanklyn, J. A., on some new ethyle-compounds containing the alkali-metals, 455.
Water, on the chemical action of, on soluble salts, 97.
Weber, R., on iodide, bromide, and chloride of aluminium, 269; on compounds of chloride of aluminium with the chlorides of sulphur, selenium, and tellurium, 444.
Weselsky, P., on the double acetates of uranium, 390.
Williams, C. G., on some decompositions of cinchonine, 89; on some of the products of the destructive distillation of Boghead coal, 119, 183, 207, 285; on the constitution of the essential oil of rue, 159; on the constitution of eugenic acid, 170; on the action of potash upon wool, 309; on the action of potash upon pelosine, 321; on some platinum bases, 346.
Williamson, Prof. A. W., on the measurement of gases in analysis, 256.
Willm, E., on phthalamine, 343.
Winkler, Dr. F. L., on the occurrence of salicylate of methyle in *Monotropa Hypopitys*, 200.
Wirz, C., on the bibasic acids of the series $C^n H^{n-2} O^8$, 247.
Wöhler, Prof. F., on boron and its affinities, 1; on some new compounds of silicium, 23; on the amount of platinum in the platinum residues, 161; on the presence of oxide of silicium in the residue obtained on dissolving pig-iron, 173; on siliciuret of manganese, 233; on the behaviour of boron to nitric oxide, 263; on a crystallized compound of chromium and aluminium, 294; on the behaviour of copper in hydrochloric gas, 310; on the nitrurets of tungsten and molybdenum, 334.
Wood-spirit, synthesis of, 33.
Wool, on the action of potash upon, 309.
Wurtz, A., on amyloglycol, 129; on lactic acid, 441; on the conversion of aldehyde into acetal, 461.
Zinc, alloys of, 296; on a new process of painting with the oxychloride of, 239.

END OF VOLUME XVI.